AMERICAN

CHEMICAL JOURNAL

IRA REMSEN
EDITOR

CHARLES A. ROUILLER
ASSISTANT EDITOR

VOL. XLIX.—JANUARY–JUNE, 1913

BALTIMORE: THE EDITOR

ESCHENBACH PRINTING COMPANY, PRINTERS,
EASTON, PA.

CONTENTS OF VOL. XLIX

No. 1

No. 2

No. 4

No. 5

REVIEWS

No. 6

REVIEWS

VOL. XLIX JANUARY, 1913 No. 1

AMERICAN

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THE ABSORPTION SPECTRA OF SOLUTIONS AS AFFECTED BY TEMPERATURE AND BY DILUTION. A QUANTITATIVE STUDY OF ABSORPTION SPECTRA BY MEANS OF THE RADIOMICROMETER

BY HARRY C. JONES AND J. SAM GUY

[This investigation was carried out with the aid of a Grant generously awarded by the Carnegie Institution of Washington.]

INTRODUCTION

An investigation on the effect of temperature on the absorption spectra of certain solutions has already been carried out by Jones and Strong.[1] The apparatus used was devised by Professor John A. Anderson,[2] who worked somewhat earlier with Jones[3] on the absorption spectra of solutions. The solutions were heated in an open vessel, and the temperature could, of course, not be raised much above one hundred degrees. It was found that even over this range in temperature the effect of rising temperature was to cause the general

[1] Carnegie Institution of Washington, Publication **130**. THIS JOURNAL, **43**, 37, 97 (1910); **45**, 1, 113 (1911).

[2] Carnegie Institution of Washington, Publication **130**.

[3] Carnegie Institution of Washington, Publication **110**, p. 20. THIS JOURNAL, **41**, 276 (1909).

absorption of any salt in water to increase, and also to cause the bands to broaden and become more intense.

The results were entirely unambiguous as far as they went, but they were limited by the boiling points of the solutions in question. Indeed, it was not possible to work quite up to the boiling point of the solution, since the change in the concentration of the solution resulting from boiling would have been too great, and there would have been too much gas formed on the quartz windows through which the light was to pass.

We wanted to study the effect of rise in temperature on the absorption spectra of solutions to as high temperatures as it was possible to go. For this purpose closed forms of apparatus devised by Anderson[1] and by Strong[2] were employed by Jones and Strong[3] for nonaqueous solutions. The apparatus consisted of a gold-plated steel tube, whose ends were closed with glass windows. This worked very well with nonaqueous solvents up to temperatures of approximately 200° C. Usually before this temperature was reached a precipitate formed in the tube, which prevented work at higher temperatures.

Some interesting results were obtained at the higher temperatures with this apparatus. The general effect of rise in temperature is to deepen the color of the solution of an inorganic salt. This is usually due to a widening of the absorption bands. For details in reference to the effect of temperature on the absorption of light by nonaqueous solutions reference must be had to the Carnegie monograph,[4] where the results in question are published in full.

The apparatus used by Jones and Strong for nonaqueous solutions did not work satisfactorily for solutions in water as the solvent. The water vapor, under the high pressure produced within the apparatus, worked its way through the layer of gold laid down on a layer of copper electrolytically,

[1] Carnegie Institution of Washington, Publication **160**, p. 28. This Journal, **47**, 30 (1912).

[2] Carnegie Institution of Washington, Publication **160**, p. 29. This Journal, **47**, 30 (1912).

[3] Carnegie Institution of Washington, Publication **160**. This Journal, **47**, 27, 126 (1912).

[4] Carnegie Institution of Washington, Publication **160**.

rusted the steel and caused the separation of the gold from the steel walls.

To avoid this, the apparatus, which was designed by Dr. Strong,[1] was made of brass and will be described in some detail later in the paper. It was plated electrolytically with gold and this adhered firmly to the brass even when the aqueous solution contained in the apparatus was heated to 200° C. We could work as satisfactorily with this apparatus with aqueous solutions as with the former apparatus with nonaqueous solutions. The work described in this paper on the absorption spectra of aqueous solutions at high temperatures was all carried out in the gold-plated, brass apparatus. The results obtained and the bearing of these results on the nature of solution will be discussed in the proper place in this paper. Suffice it to say here that the effect of temperature up to 200° on the absorption spectra of aqueous and nonaqueous solutions has now been studied pretty extensively on a large number of salts and a fairly large number of solvents.

The effect of dilution on the absorption spectra of solutions was taken up with the following idea in mind. It was long a question as to what is the nature of the absorber of light, say in aqueous solutions. It was at one time supposed that chemical molecules are the absorbers, since these were regarded as the ultimate units in solution. It was supposed that the molecules were thrown into resonance by certain wave lengths of light, and these were, consequently, stopped, while the remaining wave lengths passed through the solution and gave to it its characteristic color.

When the theory of electrolytic dissociation was proposed in 1886, the view as to the nature of solutions of electrolytes underwent a serious change. When electrolytes were dissolved in water, or in any other dissociating solvent, they dissociated into charged parts or ions, and these were the ultimate units in solution. If the solution was fairly concentrated we had both ions and undissociated molecules in the solution, and the question in such cases was, which is the absorber?

[1] Carnegie Institution of Washington, Publication **160**. This Journal, **47**, 30 (1912).

It was further recognized that a dilute solution of a salt often has very different color from a concentrated solution; and, moreover, solutions of nonelectrolytes are often colored, i. e., have the power to absorb certain wave lengths of light and to allow others to pass on through. It was supposed then that molecules have the power to absorb light, and ions also have absorbing power. When a concentrated and a dilute solution of an electrolyte had the same absorption spectrum—the same color—it was supposed that the chemical molecule and the ions resulting from it had the same absorption. When the dilute solution had a different color from the concentrated solution, it was supposed that the ions were the chief absorbers of light. And since it frequently happens that a dilute solution of an electrolyte has a very different color from a more concentrated solution, it was supposed that in dilute solutions of electrolytes the ions are the chief absorbers of light; since in very dilute solutions of electrolytes there are mainly ions and practically no molecules present, it is obvious that in such solutions it is not the molecules which are absorbing light. It must be the ions, since these are the only units present, or something contained within the ions. This was the view of absorption of light introduced by the theory of electrolytic dissociation.

We have now gone much farther than this. We now know that the ions are not the ultimate units in a solution of an electrolyte. The simplest ion is very complex. It is made up of a large number of electrons, which are unit negative charges of electricity. There is every reason to-day to believe that the electrons are the real absorbers of light, are the units which are thrown into resonance by the various wave lengths of light. Granting this, there is still a difference between an ion and the atom or atoms from which it was formed. An ion contains one or more free electrons within it, i. e., one or more negative charges than would correspond to the positive electricity within the atom. It would be interesting to know whether the free electron or electrons upon the ion have anything to do with its power to absorb light. This can be tested by studying the absorbing power of molecules and then the

absorption of light by the ions which are formed when these molecules dissociate. It was with this idea in mind that the second chapter of the work described in this paper was undertaken.

A concentrated solution of a salt contains many molecules, and if the solution is sufficiently concentrated there are chiefly molecules and only a few ions present. As the dilution is increased the dissociation increases, the number of molecules becomes less and less and the number of ions greater and greater. The problem then is to photograph the absorption spectrum of a very concentrated solution of a salt, the layer being, say, 0.5 cm. deep. Then take the spectrum of a more dilute solution of the same salt; if the dilution is increased one hundred times the depth of layer used would be fifty cm. Under these conditions there would be the same number of parts of dissolved substance in the path of the beam of light; in the second case, there would be more ions and less molecules than in the first. By comparing the two spectra we could see whether there is any difference between the absorbing power of ions and molecules, i. e., whether the free electrons upon the ions have anything to do with their power to absorb light We then took another step, increasing the dilution of the second solution five times and also increasing the depth of the layer of the solution through which the light passed five times, i. e., making the depth 250 cm. This second diluting still further reduced the number of molecules present and increased the number of ions. By comparing the three spectrograms we ought to be able to say whether molecules and ions have the same or different resonance with respect to light waves, and, if it is different, to point out in what the difference consists. This would then enable us to determine whether the free electrons upon the ions played any part in the absorption of light.

We shall see that ions have somewhat different absorbing powers from molecules, and in what this difference consists will appear later from the text and from the plates.

The work done on the absorption spectra of solutions by

Jones and Uhler,[1] Jones and Anderson,[2] and Jones and Strong,[3] which extended over five years, and in which some 6000 solutions were studied, all involved the photographing of the various spectra. In this way the positions of the various absorption lines and bands were determined.

A question even more fundamental than the positions of the lines and bands is their intensities, and the relative intensities of different parts of the same band. The photographic method gave only a means of dealing qualitatively with this problem. Some general idea could be gained of the relative intensities of the various lines and bands on the photographic plate, but these changed with the time of exposure, the intensity of the light used and with other conditions, so that we were able to learn very little about the intensities of the various lines and bands by means of the photographic method.

Further, the photographic plate is sensitive only between the wave lengths 2000 Å.U. and 7600 Å.U., which is a comparatively small part of the spectrum. It is especially important to work also into the region of the infrared.

A method was used which dealt quantitatively with the intensities of the various lines and bands. This same method, instead of being limited by the above-named wave lengths, could be used down into the infrared to wave lengths as great as 20000 Å.U. to 30000 Å.U. Indeed, the method can be used for even greater wave lengths, if solvents can be found that are transparent to the longer waves. This method involves the use of the radiomicrometer.

The description of the instrument which we built, the method of work, and the results thus far obtained, will be given in the third section of this paper.

THE ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS AS AFFECTED BY TEMPERATURE

Jones and Strong[4] studied the effect of temperature on the

[1] Carnegie Institution of Washington, Publication **60**. This Journal, **37**, 126, 207 (1907).

[2] Carnegie Institution of Washington, Publication **110**. This Journal, *Loc. cit.*

[3] Carnegie Institution of Washington, Publications **130** and **160**. This Journal, *Loc. cit.*

[4] This Journal, **47**, 27, 126 (1912).

absorption spectra of various nonaqueous solutions up to nearly 200°. The solutions were usually heated until a precipitate formed, which cut off the light and prevented work at still higher temperatures. Some work was also done by Jones and Strong on the effect of temperature on the absorption spectra of aqueous solutions. This was, however, not large in amount and did not extend to very high temperatures.

The reason that the work was not pushed to higher temperatures, with aqueous solutions, was that the form of apparatus then in use did not admit of it. This consisted of a steel tube,[1] lined on the inside with copper and plated with gold on all of the inner surfaces. This worked very satisfactorily with nonaqueous solutions, the gold plate adhering firmly to the copper, which, in turn, remained adherent to the steel.

When an aqueous solution was heated in the apparatus from 100° to 200° the result was unsatisfactory. The water, under the high pressure, forced its way through the copper and the gold and rusted the iron, as has already been stated. The result was that the copper, with the gold, separated from the steel, and the solutions, after heating for a time, gave the iron reaction. This apparatus had the further disadvantage that when a precipitate formed with rising temperature it was necessary to open the entire apparatus and remove the glass ends in order to clean them.

To overcome these difficulties the following form of apparatus (Fig. A) was constructed and used to study the effect of rising temperature on the absorption spectra of aqueous solutions.

The quartz ends are fastened into the ends E'. The plunger P has guide grooves instead of guide pins. A part of the plunger is provided with screw threads for removing it. The entire cap is removed from tube T by unscrewing E', during which the quartz end is untouched. When the ends are removed the quartz window can be easily cleaned. Gold washers were inserted between T and E' and between E' and U.

[1] This Journal, **47**, 30 (1912).

The general arrangement of the apparatus is also shown in Fig. A. The cell is kept in a horizontal position so that any bubbles that may form will rise in the side tube. The spectroscope, containing the grating *G*, photographic plate holder *C*, and slit *S*, being kept vertically, a 45° quartz prism was used to change the horizontal beam of light into a vertical beam, the beam being totally reflected by the hypothenuse surface of *O*. The source of light *N G* (Nernst glower) or *S G* (spark gap) was focused by the concave speculum mirror *M* on the slit *S*. A similar arrangement was used for the fused silica cell. *D T S* is a double throw switch, by means of which either the Nernst glower or the spark gap may be thrown in circuit. *B* is a ballast. *R* is a variable resistance, by means of which the current in the Nernst glower, as shown by the ammeter *A*, may be kept constant. *O C* is an oil condenser. *I C* is an *X*-ray induction coil and R_2 is a resistance in the primary circuit of this coil. In a recent paper Merton[1] states that he has studied the effect of pressure on the absorption spectra of solutions. This was studied here and the results published in THIS JOURNAL;[2] the quotation of a paragraph from our earlier paper will show what was found:

"Some preliminary tests were made with the cells at high pressures. The Cailletet pump belonging to the University was used for this purpose, the cell being made so as to fit into this pump. It was not at all difficult to obtain pressures of 200 atmospheres with water and alcohol solutions. Spectrograms were made of the absorption spectra of neodymium solutions under pressures as high as 275 atmospheres. *No effect of pressure was detected.* The work at high pressures is easier than at high temperatures, on account of the fact that there is an expansion of the cell due to heating.

It should be stated that in all of the work on absorption spectra which has been carried out in this laboratory for the past seven years, a grating spectroscope has been used. The arrangement of the heated cell, the grating, photographic plate, etc., will now be discussed.

[1] P. Roy. Soc., (A) **87**, 146.

[2] Vol. **47**, page 32, January, 1912.

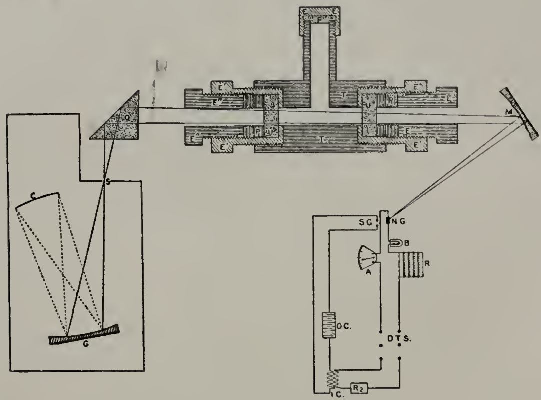


Fig. A.

Discussion of Some of the Results Obtained

The description of a few of the spectrograms obtained is given in the following pages. The plates as a whole will probably be published in the near future as a monograph by the Carnegie Institution of Washington.

The Making of a Spectrogram

The apparatus used throughout the entire study of the effect of high temperature has already been discussed. Two cells were used, one ten cm. and the other one cm. in length, both having the same general design and differing only in length.

The cell, placed in a suitable bath for keeping the temperature constant, was arranged as indicated in the diagram and the source of light so located that the rays, reflected from a concave mirror, passed longitudinally through the cell and formed an image of the Nernst glower on the slit of the camera. The position of the prism is so adjusted as to fill the grating uniformally with light. Holding the eye directly above the grating, in a position later to be occupied by the photographic plate, we could easily tell when the proper light was falling upon the grating. When the cell was in its proper adjustment the lights were extinguished and the photographic plate inserted. With the plate in position, the light was turned on and an exposure made at room temperature. The position of the plate was then moved a given distance, and the temperature of the cell raised very slowly, this process being repeated at intervals of about 20° or 25°.

It is clear that, with such pressures as are developed by heating water to 200°, it is very difficult to obtain a tight joint between glass and metal. This difficulty, however, has been partially overcome by the special form of apparatus designed by Dr. Strong and described elsewhere in this paper. We were not able to secure a closing that would hold above 200°, but once a good closing was secured it was not necessary to remove the ends for several operations.

Great care had to be taken in heating the cell, on account of the difference in expansion of the glass ends and the metal

in contact with them. When the temperature was raised more than 40° an hour the glass ends usually broke. At such high temperatures as we were employing the glass was rapidly attacked by the water and afterwards, when we were using the clear uviole glass, a single heating rendered the glass ends almost opaque, especially if they were allowed to stand any length of time.

It was found that in many cases precipitates would appear in the cell at a temperature slightly above 100°. This precipitate, however, formed rapidly, once it began, and almost as quickly disappeared. By properly regulating the intervals at which exposures were made, the effect of the precipitate could be avoided; hence this effect does not appear on any of the strips photographed.

It is probable that at first slight hydrolysis took place, as

$$2NdCl_3 + 3H_2O \longrightarrow 2Nd(OH)_3 + 3HCl$$

The presence, then, of a slight excess of hydrochloric acid would hinder the reaction in the direction indicated above by the arrow. Since most hydroxides lose water at temperatures above 100°, it is possible that the following reaction would take place:

$$2Nd(OH)_3 \longrightarrow Nd_2O_3 + 3H_2O$$

The neodymium oxide, being heavy and very slightly soluble in water, settles to the bottom of the cell, and the solution clears up. In this way, it is evident, our solution becomes slightly more dilute as the temperature is raised, but this would lessen the number of absorbers in the path of the beam of light, and thereby produce a narrowing of the bands; it could only decrease the effect indicated in the films. This antagonistic influence could certainly not cause a widening of the absorption bands with rise in temperature.

Neodymium Chloride in Water (*see Plate I*)

The solution whose spectrum is given in Section *A* was saturated, the depth of absorbing layer being 1 cm. The temperatures, beginning with the strip nearest the numbered

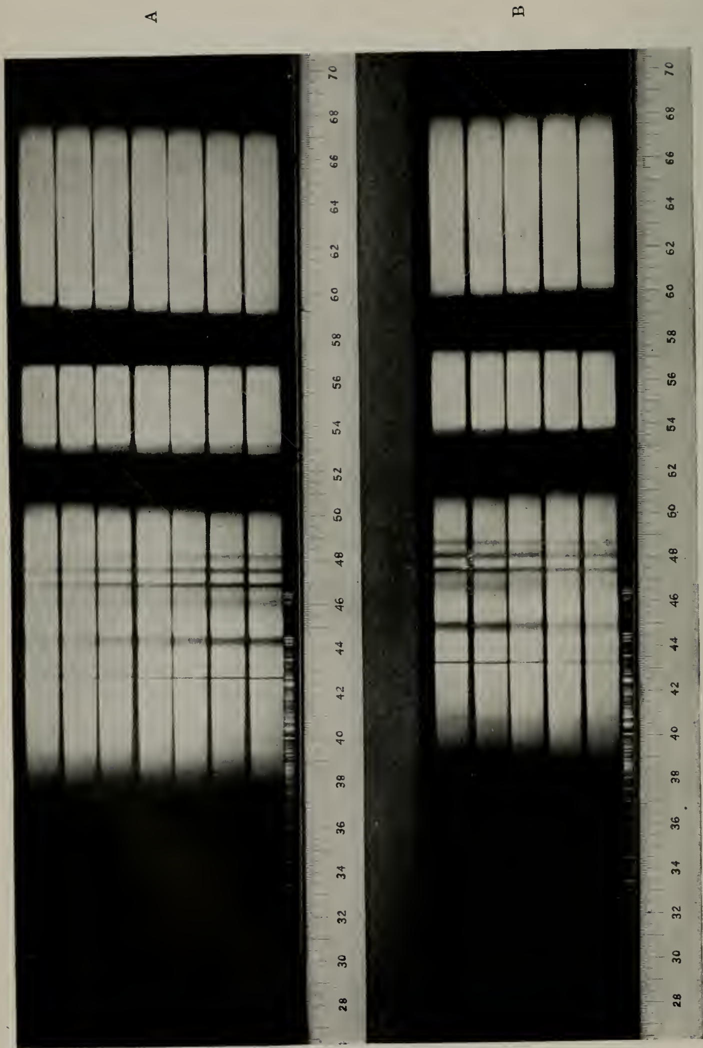


Plate I

scale, were 20°, 45°, 70°, 95°, 115°, 140° and 165°, respectively.

Absorption bands which are unchanged by the range of temperature from 20° to 200° appear at λ3800, λ4025, λ4200, λ4325, λ4440, λ4600, λ4690, λ4750 and λ4820.

The double band from λ5050 to λ5270 is only slightly affected, if at all.

The two most interesting absorption bands are those whose centers are near λ4275 and λ5800. The former of these in Strip 1 is very sharp and intense, though only a few Å.U. wide. Both edges were well defined. As the temperature is raised the violet edge remains very sharp, while a rapid shading off of the red edge takes place. At a glance the band appears to be less intense in the higher temperature strips, but on close examination it is seen to be more diffuse, the red edge diffusing over a range of about 20 Å.U. at the highest temperature. This is exactly in accord with what Jones and Anderson[1] had found. They showed that when the number of molecules in the path of light was kept constant, this band remained practically constant, while it has been shown by Jones and Anderson and by ourselves that this band changes with dilution, being more intense in the most concentrated solution.

The λ5800 band is affected most by temperature as well as by dilution. In Strip 1 this band is about 200 Å.U. wide, and increases regularly in width as the temperature is raised, until at the highest temperature the width is over 250 Å.U., or there is a total widening of 50 Å.U. The violet edge remains perfectly sharp, while the shading is towards the red end of the spectrum.

It occurred to us that whatever effect might be produced by a rise in temperature, if it was a true temperature effect, the reverse should happen when the solution was allowed to cool.

With this in view *B* was made. The concentration of the solution and the depth of layer photographed in Section *B* were exactly the same as in *A*. In fact, the identical solution

[1] Carnegie Institution of Washington, Publication **110**.

was used. As soon as the film *A* had been exposed with rising temperature, it was removed from the camera and developed. Without even allowing the cell to cool, another film was placed in the camera and Section *B* made with falling temperature. In *B* the temperatures were 165°, 140°, 115°, 95° and 70°, the highest temperature being nearest the numbered scale.

A study of the original film shows changes only in bands $\lambda 4275$ and $\lambda 5800$; and this change is exactly the reverse of that shown by these same bands in *A*. The $\lambda 4275$ band appears in Strip 1 with a sharp violet edge and shading off toward the red over a range of 15 or 20 Å.U. As we pass to the succeeding strips in the direction of falling temperature the red edge becomes sharper and sharper until, in Strip 5, which represents the lowest temperature, the band assumes its normal sharp edge on the red side and covers less than ten Å.U. The $\lambda 5800$ band narrows uniformly from the red end, as the temperature falls, the total narrowing being about 40 Å.U.

Neodymium Bromide in Water (see Plate II)

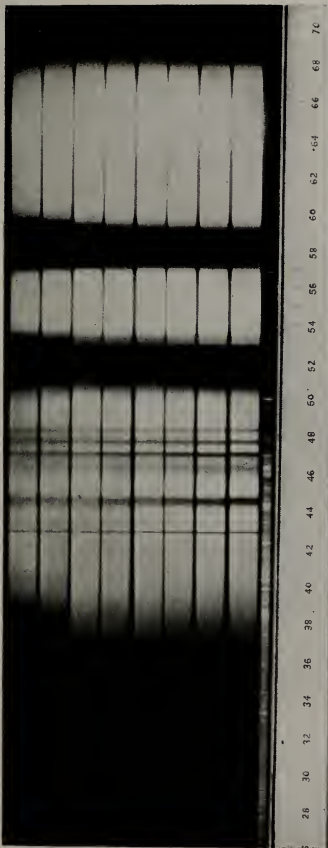
The concentration of the solution used in making the negative for *A* was 1.66 normal; the depth of cell, 1 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 120°, 140°, 175° and 190°, respectively.

This plate seems to have had just the proper length of exposure for the given concentration, and every known neodymium absorption band appears on the negative in excellent condition. With the bromide, as with the chloride discussed in Plate I, only $\lambda 4275$ and $\lambda 5800$ show changes with rise in temperature. The $\lambda 4275$ band, which has both violet and red edges sharp in Strip 1, feathers out toward the red end of the spectrum as the temperature is raised.

The $\lambda 5800$ band widens toward the red as much as 60 Å.U.

The concentration of solution used in making *B* was 0.166 normal, one-tenth that of *A*; the depth of absorbing layer was 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115° 135°, 155°

A


70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28

B

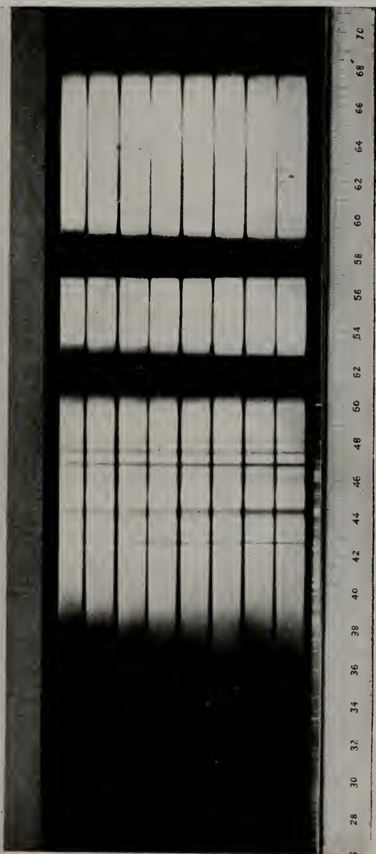

70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28

Plate II

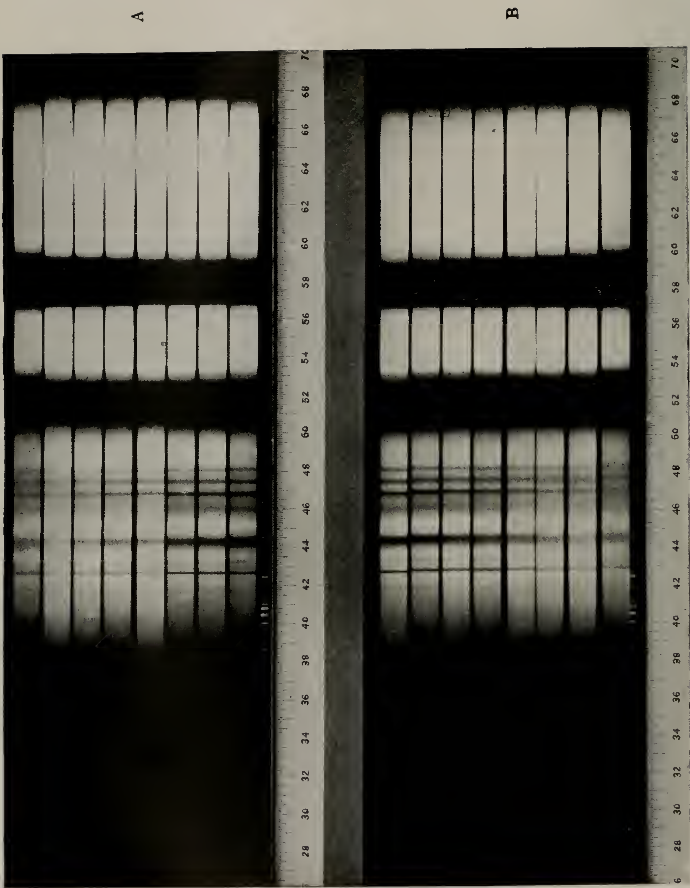


Plate III

and 190°, respectively. This is probably the best negative produced in this part of the work, and the bands $\lambda 4275$ and $\lambda 5800$ show well the characteristic changes spoken of above. The widening of band $\lambda 5800$, though well marked, is not so great as in A, the total change being about 40 Å.U., as compared with 60 Å.U. in the former.

If such a band be due to molecules this is what we should expect, since, B being a more dilute solution, the total number of molecules is less than in A. Hence, any change associated with molecules would be more clearly apparent in A.

This is in accord with changes produced in this same band by dilution.

Neodymium Nitrate in Water (*see Plate III*)

The concentration of the solution used in making the negatives of A was one-tenth of saturation, the depth of absorbing layer 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95° 115°, 140°, 165° and 190°.

Aside from the slight tendency for all the absorption bands to become a little more diffuse, though not more intense, at the higher temperatures, there is no marked change in any band except $\lambda 4275$ and $\lambda 5800$. The former of these, as we go toward the higher temperatures, remains perfectly sharp and constant on its violet edge, while there is a regular shading towards the red end of the spectrum. Again, the greatest change takes place in band $\lambda 5800$, the violet end remaining fixed and the red edge widening between the first and last strips to the extent of about 50 Å.U. All the exposures of this plate were made as the temperature of the cell was raised.

The identical solution used above was photographed in B—the cell, intensity of light source, and all of the apparatus, remaining unchanged, the only difference being that the exposures of B were made at regular intervals as the temperature of the cell was *lowered*. The temperatures of the successive strips in B were, beginning with the strip nearest the numbered scale, 190°, 165°, 140°, 115°, 95°, 70°, 45°, 20°.

The original films show A and B to be exactly the reverse

of each other. Just those changes produced in *A* by a rise in temperature are reversed by the corresponding fall of temperature in *B*. Of course, this is only qualitative, since we can establish no definite quantitative relations from the photographic plates. In order to do this, energy measurements must be made, not only on each band, but on different parts of the same band. Such work is now in progress. This, of course, would be very difficult to do with a narrow band like λ4275, but should be comparatively simple with band λ5800.

Band λ4275, which, in Strip 1, appears broad and hazy on its red edge, gradually acquires the characteristic sharp intense edges as the temperature falls, until, in Strip 8, it is only about 8 Å.U. wide. The total change in band λ5800 is a narrowing of about 60 Å.U. There is no sudden or decided change between any two successive strips, but, on the contrary, so far as the photographic plate is able to show, the change is a gradual one.

Neodymium Acetate in Water (see Plate IV)

In Plate IV we have photographed the change in the absorption bands of neodymium acetate, produced by rise in temperature, Section *A*, and by the corresponding lowering of temperature, Section *B*. The concentration of the solution used for both negatives was one-tenth of saturation; the depth of absorbing layer, 10 cm.

The temperatures of the strips in *A*, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 120°, 140°, 160°, 190°. This negative shows changes in bands λ4275 and λ5800; the former, as in the other plates on the study of the effect of temperature, shows a marked shading toward the red, while the remainder of this band virtually remains fixed. The λ5800 band widens rapidly towards the red, as the temperature is raised, the total amount being about 80 Å.U. All the absorption bands with the acetate are more intense and broader than for the same concentration of any of the other salts of neodymium studied. The acetate is not nearly so soluble as the other salts, nor is the dis-

A

B

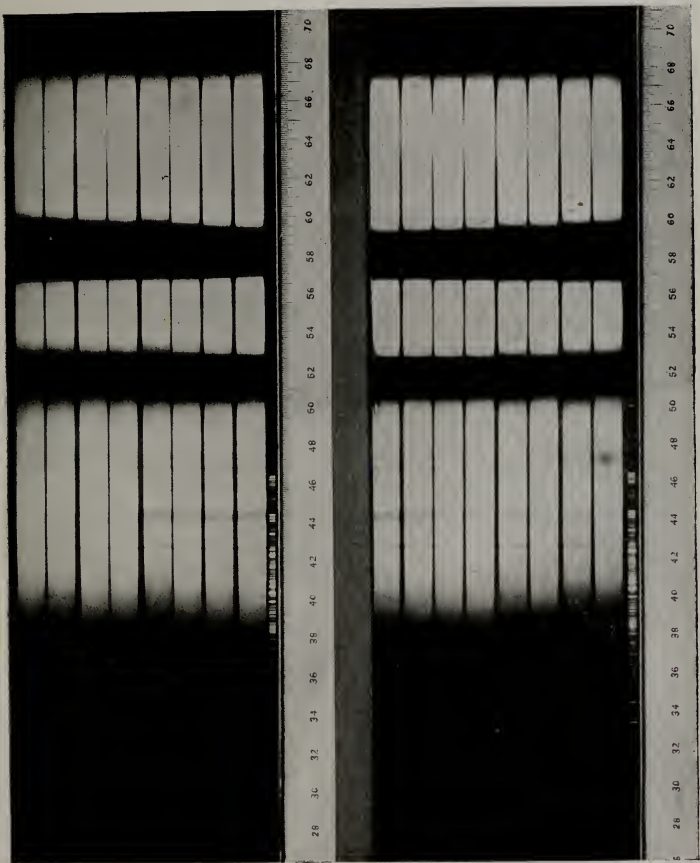


Plate IV

A

B

Plate V

sociation so great, yet we find in *A*, which is the spectrogram of a one-tenth saturated solution of neodymium acetate, greater changes than for the saturated solution of the chloride. This is in accord with the results obtained from the effect of dilution: this, it will be seen, was greatest with the acetate. This tends to strengthen the view that the bands λ4275 and λ5800 are in some way associated with the molecules.

In *B* of this plate there is given the spectrogram of the same solution as the temperature was lowered. The temperatures, beginning with the strip nearest the spark spectrum, were 190°, 165°, 145°, 125°, 100°, 75°, 50°, 25°; the cell and arrangement of apparatus were the same as in *A*. The negative shows changes the reverse of those discussed in Section *A*. The λ4275 band gradually assumes the sharply defined edges as the temperature falls, and Strip 8 of *B* corresponds exactly to Strip 1 of *A*. In a word, there has been no permanent change produced by heating the solution. This change in the width of the absorption bands could not have been produced by any substance dissolved from any parts of the apparatus, as there is no reason to suppose that this should disappear as the solution was cooled. It seems, then, that the broadening is solely a temperature phenomenon.

Praseodymium Nitrate in Water (*see Plate V*)

The concentration of the solution used in making *A* was 2.6 normal; the depth of cell, 1 cm. The temperatures, beginning with the strip nearest the numbered scale, were 12°, 32°, 52°, 72°, 92°, 112°, 125° and 145°, respectively.

In the ultraviolet the absorption extends to about λ3500 in Strip 1, but rapidly increases as the temperature is raised, until in Strip 8 there is complete absorption as far as λ3800.

There is a very intense double absorption band from λ4350 to λ4725 with faint transmission near λ4540. This transmission rapidly decreases as the temperature is raised, and entirely disappears at a temperature slightly above 100°. The λ4650 band widens toward the red end about 25 Å.U. Band λ4825 shows a total widening of about 30 Å.U. over the range of temperature studied. The orange band near λ5900 shows a uniform total widening of about 25 Å.U.

From this plate it is seen that none of the praseodymium bands show very marked change with rise in temperature. It may be stated that, at this concentration, all of them become slightly wider at the higher temperatures.

In Section *B* of this plate is given the spectrogram of a 0.26 normal solution of the same salt, the depth of the absorbing layer being 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, 135° and 165°, respectively.

There appear on this plate bands which have their centers near $\lambda 4425$, $\lambda 4650$, $\lambda 4825$ and $\lambda 5900$; the ultraviolet absorption bands near $\lambda 3500$. None of these bands show any appreciable change over the range from 20° to 165°.

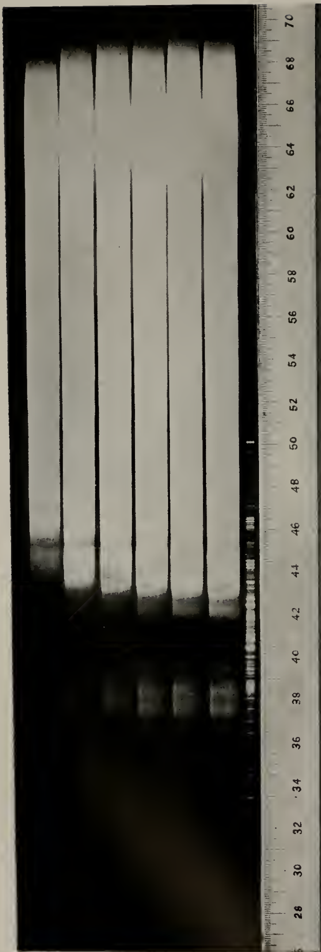
The plate which was used to study the effect of dilution upon this same salt reveals the fact that only in the most concentrated solutions were the bands affected at all, while in the dilute solutions all the bands remained unchanged. It is seen from Plate V, discussed above, that temperature also has a slight effect only in the concentrated solutions, while in the dilute solutions the bands remain unchanged. In a word, rise in temperature and decrease in dilution produce the same effect upon solutions of praseodymium nitrate.

Uranyl Nitrate in Water (*see Plate VI*)

The concentration of the solution used in making *A* was 0.2 normal, the depth of layer being 1 cm. The temperatures, beginning with the strip nearest the spark spectrum, were 20°, 40°, 60°, 80°, 100° and 120°, respectively. In every strip the exposure to the entire spectrum was made for thirty seconds, a screen cutting off all wave lengths beyond $\lambda 4500$ was inserted and the ultraviolet end exposed an additional eight minutes.

Since all the uranyl bands occur in the violet and ultraviolet end of the spectrum where the general absorption is greatest, due to precipitates formed by heating the solutions, etc., it was found very difficult to obtain satisfactory results. So far as this plate shows there is no decided change in any particular band. The entire series seems to widen as the tem-

A



B

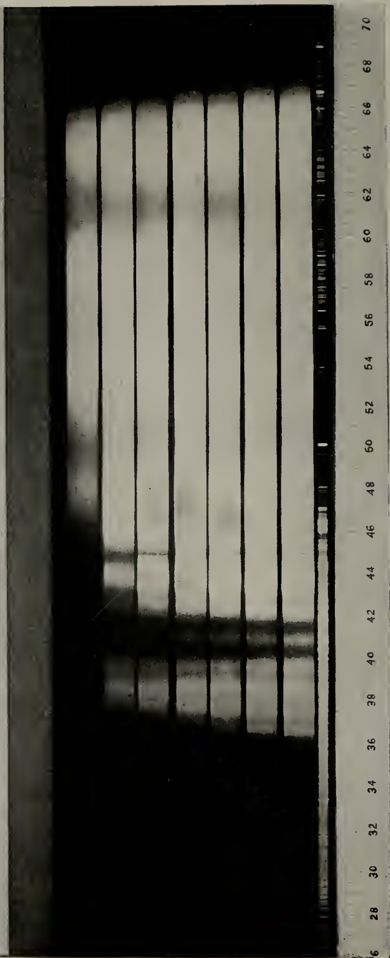


Plate VI

perature is raised, and at the same time the center of the band is slightly shifted toward the red end of the spectrum. The general absorption, ending near $\lambda 3500$, in Strip 1, advances rapidly toward the red as the temperature is raised. The broad diffuse edges of all the bands shade uniformly into each other, until at the highest temperature they appear as one broad hazy absorption band, extending from $\lambda 3800$ to $\lambda 4300$. At least a part of this is due to general absorption.

In Section *B* is given the absorption of a 0.02 normal solution of uranyl nitrate, the depth of absorbing layer being 10 cm. The red end of the spectrum, beyond $\lambda 4500$, was exposed eight seconds, while the ultraviolet below $\lambda 4500$ had an exposure of three and one-half minutes to the same source of light. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, 140° and 165°, respectively. There are eleven bands occurring between $\lambda 3500$ and $\lambda 4600$. As the temperature is raised all the bands become more diffuse and broader. The band whose center is near $\lambda 4180$ seems to be most affected. The red edge of the band shades toward the red end of the spectrum as much as 25 Å.U. The effect produced on this band by elevated temperatures is more marked than in any of the other bands. There is very broad and hazy absorption around $\lambda 5100$, $\lambda 5600$ and $\lambda 6200$. This increases with rise in temperature.

It has been found very difficult to give an exact description of what takes place in any uranyl band as the temperature is raised, since the edges of the bands are so hazy and the general absorption so marked in the region of the spectrum at which these bands occur. Only the general statement can be made that all uranyl bands become more diffuse with rise in temperature, and in one case, i. e., the band $\lambda 4165$, there is a decided shading on the red edge.

Uranyl Sulphate in Water (see Plate VII)

The concentration of the solution used in making *A* was 0.166 normal and the depth of cell 1 cm. The respective temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 90°, 115°, 135°, 155° and 185°. The

part of the spectrogram above $\lambda 4550$ was exposed 40 seconds, while below that wave length the exposure was ten minutes. The apparent band extending entirely across the spectrogram near $\lambda 4550$ is the edge of the screen used in making the long exposure on the violet end of the spectrogram, and must not be confused with an absorption band.

Absorption bands $\lambda 4175$ and $\lambda 4325$ have their centers shifted towards the red end of the spectrum about 25 Å.U. The red edges of bands $\lambda 4325$ and $\lambda 4550$ shade rapidly toward the red. The well marked band $\lambda 4750$ remains unchanged throughout the spectrogram.

The encroachment of the general absorption in the ultraviolet towards the red causes band $\lambda 3625$ to disappear above the fourth strip while band $\lambda 3750$ is scarcely visible above Strip 5. All bands below $\lambda 4500$ become very diffuse as the temperature is raised, and at the highest temperature are hardly more than a single broad hazy absorption band, extending from $\lambda 4000$ to $\lambda 4400$.

Section *B* is the spectrum of a 0.02 normal solution of uranyl sulphate, the depth of absorbing layer being 10 cm. The respective temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, 140° and 165°. The exposures were eight seconds in the visible part of the spectrum and an additional exposure of four minutes to the ultraviolet.

The same changes described in *A* take place here, i. e., a strong general absorption in the ultraviolet beyond $\lambda 3500$, and increasing toward the red as the temperature is raised. The most marked widening is in bands $\lambda 4100$, $\lambda 4200$ and $\lambda 4350$. Each of these bands has its center shifted slightly toward the red. Such is also the case with the red edge of band $\lambda 4600$. The $\lambda 4750$ band remains fixed throughout the spectrogram. The very broad hazy bands around $\lambda 5100$, $\lambda 5600$ and $\lambda 6200$ appear and are not appreciably affected by changes in temperature.

THE EFFECT OF DILUTION ON THE ABSORPTION OF LIGHT BY SOLUTIONS

The question as to the effect of dilution on the power of solu-

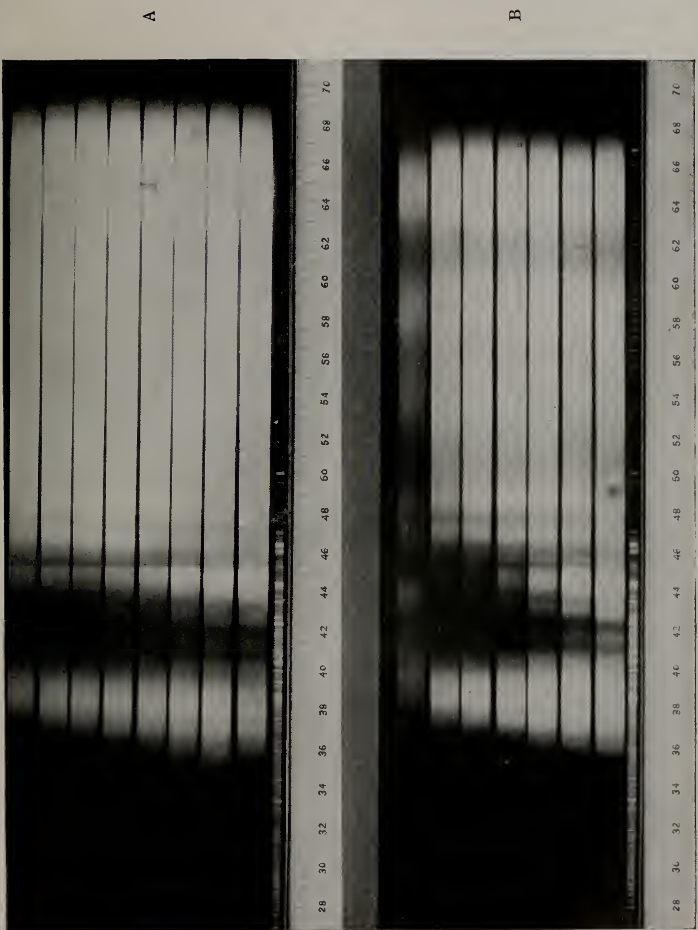


Plate VII

tions to absorb light is an old one. This question became especially prominent at the time the theory of electrolytic dissociation was proposed. In dilute solutions of electrolytes there are practically only ions present, very few molecules existing as such. All of the properties of such solutions are the properties of the ions contained in them. Therefore, the power of these solutions to absorb light must be due to the ions present in them. This was the reasoning in vogue, and the conclusion drawn.

It was at the same time freely recognized that molecules in solution have the power to absorb light. This was shown by the fact that solutions of nonelectrolytes, or completely unionized substances, are often colored; and color in solution means selective absorption of light.

The result of the conclusion drawn from the theory of electrolytic dissociation was that an enormous amount of work was done on the absorption spectra of dilute solutions of both electrolytes and nonelectrolytes. Ostwald carried out an elaborate investigation on the relation between color and dissociation, and published the work under the title "Ueber die Farbe der Ionen."[1] A large number of salts were brought within the scope of this investigation: Salts of an acid having a colored anion, with colorless cations. This is illustrated by the various permanganates, hydrogen, sodium, ammonium, magnesium, zinc, cadmium, etc. Ostwald showed that these salts of any given acid had essentially the same spectra. In a similar manner he studied salts of fluorescein, eosin, iodoeosin, rosolic acid, diazoresorcinol, etc. Ostwald then reversed the process and compared the salts of a given colored base with colorless acids. Thus, he studied the salts of *p*-rosaniline with acetic, chloric, benzoic, hydrochloric, nitric, butyric, salicylic, lactic, etc., acids, and found practically the same absorption spectra for all of these salts.

From the standpoint from which he undertook his investigation, Ostwald may be said to have solved the problem of the rôle of ions in the absorption of light, as far as that could be done with the prism spectroscope.

[1] Z. physik. Chem., **9**, 579 (1892).

The problem that we studied was of a different nature. It had to do with the absorption spectra of ions relative to that of the molecules from which they were formed. Some earlier work of Jones and Anderson[1] had shown that if molecules have different action on light from ions, the difference is slight. Indeed, so slight that there would be no hope of detecting it by ordinary means, even with a grating spectroscope. This problem was attacked in the following manner:

Making a Dilution Spectrogram

Before entering upon a detailed discussion of the spectrograms it is wise to state briefly the method used in making any given spectrogram. Throughout all the work done on the effect of high dilution on absorption spectra, under the conditions of Beer's Law, only three exposures were made for any given spectrogram, i. e., only three dilutions were compared. The depths of cell in all cases were 0.5 cm., 50 cm. and 250 cm., the dilution being increased one hundred times between the first two solutions and five times between the last two, or a total dilution of five hundred times between the first and last solution. Smaller depths of cell than five mm. were not used on account of the large percentage error in measuring such depths.

Much difficulty was experienced in getting sufficient light through the longer cells to fill the grating completely, nor was this possible unless the tube containing the solution was constantly moved backwards and forwards so that the image of the source of light was moved along the slit of the camera. By such a procedure the surface of the grating could be illuminated fairly uniformly, and the exposures gave good results on the photographic plate as is shown by the spectrograms.

In order to insure complete illumination of the grating a uniform procedure was adopted. The longest cell, containing the most dilute solution, was first placed in position, the light passed through and the image of the Nernst glower sharply focused on the slit of the camera in such a manner as to throw

[1] Carnegie Institution of Washington, Publication **110**.

as much light as possible on the grating. By holding the eye in the position later to be occupied by the photographic plate, we could easily tell when the grating was properly illuminated.

After everything was properly adjusted the lights were extinguished and the plate inserted in the camera. Great care was taken not to move any parts of the apparatus, the camera was closed, the source of light again turned on, and the exposure made. It is clearly seen that in making any spectrogram, using three cells differing in length so markedly, we virtually had three different sources of light, and, consequently, the length of exposure sufficient to give comparable results on the photographic plate had to be determined by a long series of experiments. In the case of the longest cell, exposures as long as several minutes were made, while with the shortest cell only a few seconds were necessary to give good clear spectrograms on the photographic plate.

The remaining procedure was essentially the same as that described by Jones and Anderson[1] and by other workers in this laboratory.

Neodymium Chloride in Water (see Plate VIII)

The concentrations of the solutions used in making the negative for *A*, beginning with the one whose spectrum is adjacent to the spark spectrum, were 2.05, 0.0205 and 0.00401 normal, respectively, the corresponding depths of absorbing layer being 0.5 cm., 50 cm. and 250 cm.

For *B* the concentrations used were 1.025, 0.01025 and 0.00205 normal. The depths of layer were the same as used in *A*. It is seen that the dilutions are just one-half that of the corresponding layers in *A*.

The concentrations of solutions used in making *C* were just half of those in *B*, i. e., 0.512, 0.00512 and 0.00102 normal. In the entire plate, as in all the dilution work, the most dilute solution is always nearest the spark spectrum.

Since very much of the finer detail and several of the narrowest bands are lost in reproducing and printing the films,

[1] Carnegie Institution of Washington, Publication **110.**

our discussion is always based upon the original photographic film. Lines will frequently be discussed which do not appear on the printed plates, but which are very clear and distinct on the photographic film.

A study of *A* shows complete absorption in the violet up to $\lambda3350$; then slight transmission for about 50 Å.U. The faint hazy band $\lambda3400$ and the well defined band $\lambda3450$–$\lambda3600$ are not affected by the change in dilution. Hazy bands appear at $\lambda3820$, $\lambda4040$ and $\lambda4200$. Their intensities do not seem to be affected by dilution. The beautiful sharp band $\lambda4275$ is slightly more intense in the most concentrated solution. The effect of dilution, if any, on the bands $\lambda4325$, $\lambda4440$, $\lambda4600$, $\lambda4690$, $\lambda4750$, $\lambda4820$ is not measurable. On the original film they appear slightly broader, but not more intense, on the third strip.

Bands which have their centers near $\lambda5100$, $\lambda5200$ and $\lambda5800$ are decidedly affected by dilution, the former two appearing distinctly as independent bands in the most dilute solution, diffuse with a single broad band with the center near $\lambda5150$. There is the greatest change between the second and third strips (in discussing any plate Strip 1 is always nearest the spark lines). The broadening of these bands, both of which have rather hazy edges, is fairly uniform, i. e., they widen both towards the red and violet ends of the spectrum.

The intense band which extends from $\lambda5690$ to $\lambda5850$ is affected very markedly by dilution, the widening being almost entirely towards the red end of the spectrum. The violet edge is hardly affected while the widening toward the red is about 50 Å.U. Here also the change in the width of the band is greatest where the change in concentration of the solution is greatest. There is a very faint band, $\lambda6225$, which appears slightly more diffuse in the most concentrated solution.

The concentrations of the solutions used in *B* are just one-half those of *A*, and it is seen that some of the smaller bands are lost while the broader ones have split into two or more smaller bands. In this film bands near $\lambda3425$, $\lambda3475$, $\lambda3520$, $\lambda3575$, $\lambda4275$, $\lambda4340$, $\lambda4450$, $\lambda4700$, $\lambda4750$, $\lambda4820$, $\lambda5100$, $\lambda5120$, show no change with dilution. The broad band $\lambda5700$–$\lambda5825$

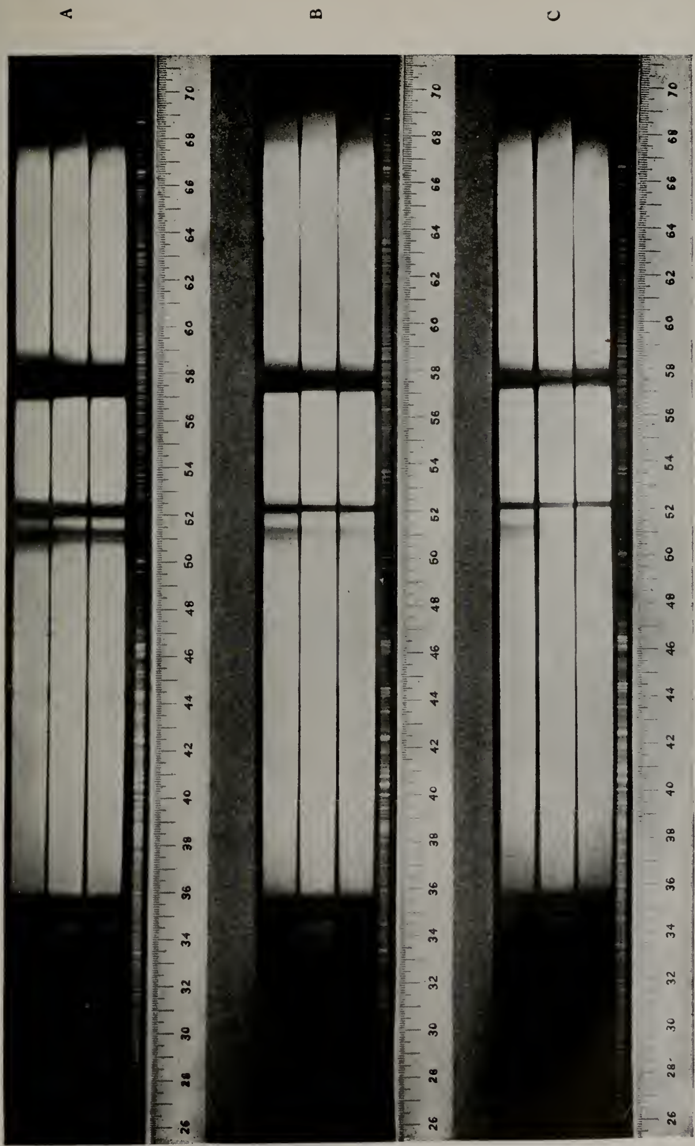


Plate VIII

A B C

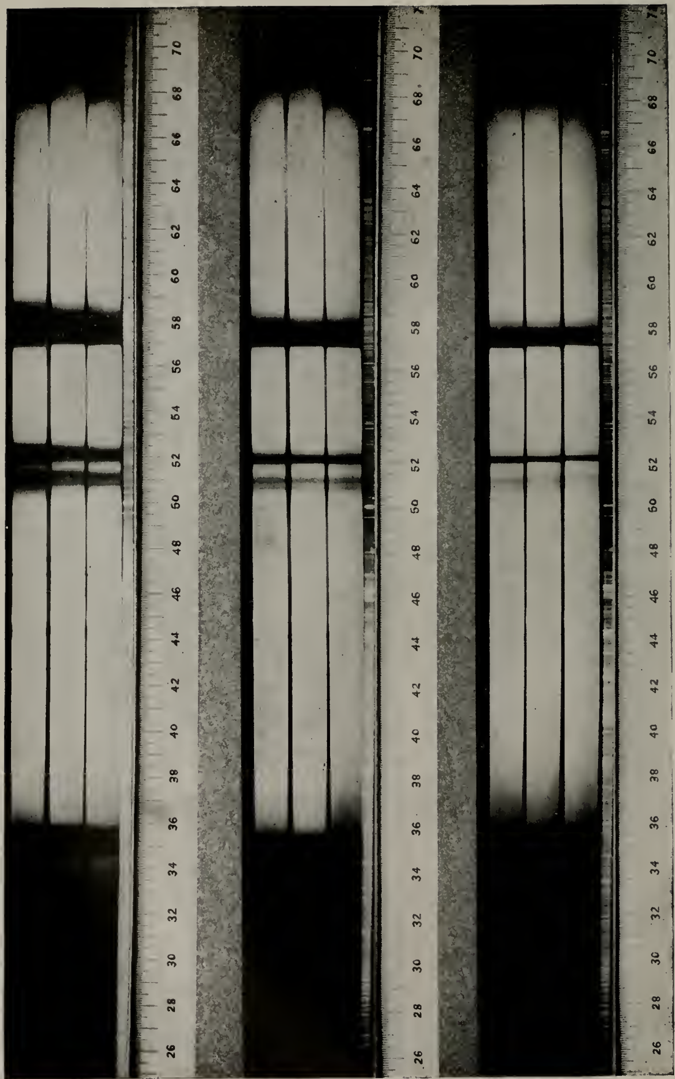


Plate IX

shows a widening of about 25 Å.U., being the only band which is changed by dilution.

C of this plate is the spectrogram of solutions twice as dilute as those of *B*. No band on this plate shows any appreciable change produced by dilution, except probably a slight widening of λ5750.

We then see, from a study of this plate, that in *A* bands λ4270, λ5100, λ5200 and λ5750 narrow with dilution, the amount of change being in the order given; that is, least in λ5100 and greatest in λ5700. In *B* there is an appreciable change in only λ5750, while in *C* none of the bands are affected by dilution.

Neodymium Bromide in Water (see Plate IX)

The concentrations of the solutions used in making Negative *A*, beginning with the solution whose spectrum is farthest from the scale, were 1.66, 0.0166 and 0.0033 normal; the corresponding depths of absorption layer were 0.5 cm., 50 cm. and 250 cm., respectively.

The concentrations used in making *B* were half of those of *A*, and those of *C* half those of *B*. The same range of cell depth was used in all three sections of this plate, viz., 0.5 cm., 50 cm. and 250 cm., respectively, beginning with the strip farthest from the spark lines. In *A* characteristic absorption bands appear at λ3400, λ3525, λ3800, λ4275, λ4450, λ4700, λ4750, λ4800, which are hardly affected by change in dilution, except for a slight increase in the intensity of band λ4275 in the most concentrated solution.

The three bands, λ5090, λ5120 and λ5210, narrow uniformly with dilution, the greatest change being between Strips 2 and 3, where the change in dilution is the greatest. With the bromide, as is seen in Plate IX, which gives the spectrogram of neodymium chloride, the effect of dilution is most pronounced in band λ5750. The shading is almost exclusively toward the red, the violet edge remaining practically unchanged. This edge shows no change between Strips 1 and 2, yet the red edge is widened as much as 30 Å.U.

In *B*, where the concentrations were 0.83, 0.0083 and 0.00166 normal, respectively, the depths of absorbing layer

were the same as used in A. There is no measurable change in any of the absorption bands except the band whose center is near $\lambda 4800$. This band shows the characteristic narrowing with dilution, as the dilution is increased. The total change is not greater than 20 Å.U. Band $\lambda 5200$ is slightly more intense in the third strip.

When we reach the dilution used in C, which is four times that of A, any change due to dilution has disappeared except a narrowing of probably 10 Å.U. between the third and second strips.

Taking Plate IX as a whole we see, first, the narrowing due to increased dilution is most marked in A, less in B, and least in C. This is seen to be the same order as their respective concentrations. Considering an individual section, we find the most pronounced narrowing where the change in dilution is greatest—that is, between Strips 2 and 3.

Neodymium Nitrate in Water (see Plate X)

The concentrations of neodymium nitrate used in making Negative A of this plate, beginning with the strip farthest from the numbered scale, were 2.15, 0.0215 and 0.00430 normal, the corresponding depths of absorbing layer being 0.5 cm., 50 cm. and 250 cm., respectively.

In discussing the absorption bands of this, as well as other plates throughout this paper, we do not attempt to give the exact position of the band in question as has previously been done by many workers; but we simply indicate the position of the band by selecting a wave length near its center. For instance, in speaking of band $\lambda 5800$, we mean that broad band extending from $\lambda 5700$ to $\lambda 5850$. This is not confusing and saves space and time in the description of any plate.

This is probably the best plate we have illustrating the effect caused by dilution. Bands that are hardly affected over the range of dilution given in A are located at $\lambda 3525$, $\lambda 3820$, $\lambda 4440$, $\lambda 4620$, $\lambda 4750$, $\lambda 4830$. The well defined band $\lambda 4275$ is more diffuse, though probably not so intense, in Strip 3. This is in keeping with the behavior of this same band as shown by other salts of neodymium, though probably a little

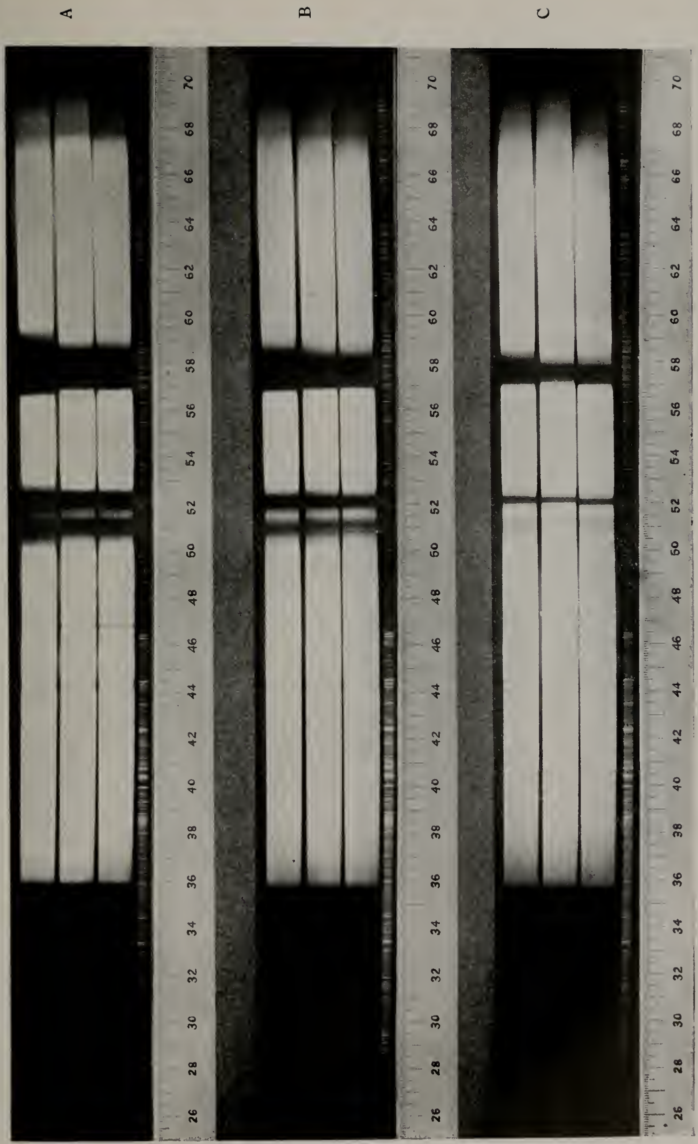


Plate X

more marked. There is faint transmission at $\lambda5100$ for about 10 Å.U. In Strip 3, representing the most concentrated solution, the bands $\lambda5090$ and $\lambda5125$ have so broadened that they became one band. The $\lambda5220$ band widens uniformly toward the red and violet as the solution becomes more concentrated.

Band $\lambda5800$, which is most affected by dilution, shows a total change of probably as much as 70 Å.U., the shading being largely towards the red. In Strips 1 and 2 the violet edge is hardly changed while in Strip 3 it is probably shifted 20 Å.U. On the original film these three strips show absolutely the same development, hence are directly comparable.

Section *B* represents the absorption of neodymium nitrate; beginning with the strip farthest from the numbered scale, the concentrations are 1.075, 0.01075 and 0.00215 normal, the corresponding depths of cell being the same as in *A*. In this section only a few bands need be discussed. Bands $\lambda5090$ and $\lambda5125$, which appear as distinct bands in Strips 1 and 2, have slightly broadened so as to form a single hazy band whose center is near $\lambda5120$. The $\lambda5750$ band narrows as much as 40 Å.U., almost the entire change being between Strips 2 and 3.

In *C*, the $\lambda5750$ band alone is noticeably changed, narrowing about 20 Å.U. from Strip 3 to Strip 2, but is not changed in the last dilution, i. e., from Strips 2 to 1.

Neodymium Acetate in Water (see Plate XI)

The concentrations of solutions used in making *A* of this plate were saturated, one-hundredth saturated, and five-hundredth saturated, the corresponding depths of cell being 0.5 cm., 50 cm. and 250 cm., respectively. The most dilute solution is nearest the numbered scale.

This plate was made with very long exposures to see if the apparent widening of the bands could be due to the difference in the amounts of light falling upon the photographic plate. In such a procedure the most concentrated solution was given the longest exposure and yet had the broader bands. It is possible to narrow any given absorption band by length-

ening the time of exposure, but this cannot account for so large a difference as is shown by Strip 3 of Section *A*. Even in this section it is seen that the third strip has wider bands than either of the other two strips of this section, notwithstanding the fact that the actual exposure of the strip is greater. Thus we see that the difference of exposure cannot account for the changes in the width of bands such as we have noted.

In Section *A* the violet group of bands in the region $\lambda3500$ came out beautifully. Such is only the case when quite a long exposure is made. Indeed, in order to show these lines well the exposure must be long enough to destroy those fine, sharp lines in the region of $\lambda3800$ to $\lambda4600$. Hence, in this plate the latter group of lines do not appear distinctly, though traces of them can be seen on the original film.

The hazy bands $\lambda3300$ and $\lambda3400$ appear on this plate and remain unchanged by dilution.

The three bands, $\lambda3460$, $\lambda3500$ and $\lambda3540$, remain perfectly constant throughout the section. Band $\lambda5120$, which appears broad and diffuse, shows no change. Band $\lambda5210$ narrows about 10 Å.U. from the third to the second strip and remains unchanged with the next dilution. The broad band $\lambda5750$ narrows about 40 Å.U. from the third to the second strips, and about 15 Å.U. with the next dilution.

The concentrations used in *B* were again just half those in *A*, the most concentrated solution being one-half saturated, with succeeding dilutions of one hundred and five times, respectively; the depths of cell, beginning with the strip farthest removed from the scale, were 0.5 cm., 50 cm. and 250 cm.

Again, only bands $\lambda5220$ and $\lambda5750$ are changed, but with the acetate the change extends farther with the more dilute solutions. In a word, the narrowing of the bands with dilution is more marked in *B* and *C* than in the case of the chloride, bromide and nitrate. The group of bands near $\lambda3500$ is not altered with dilution.

The concentrations used in *C* are again half of those in *B*, and the corresponding depths of cell the same as used throughout this plate. Their respective sequence is the same. In this spectrogram only band $\lambda5750$ changes, and, indeed, this

A B C

Plate XI

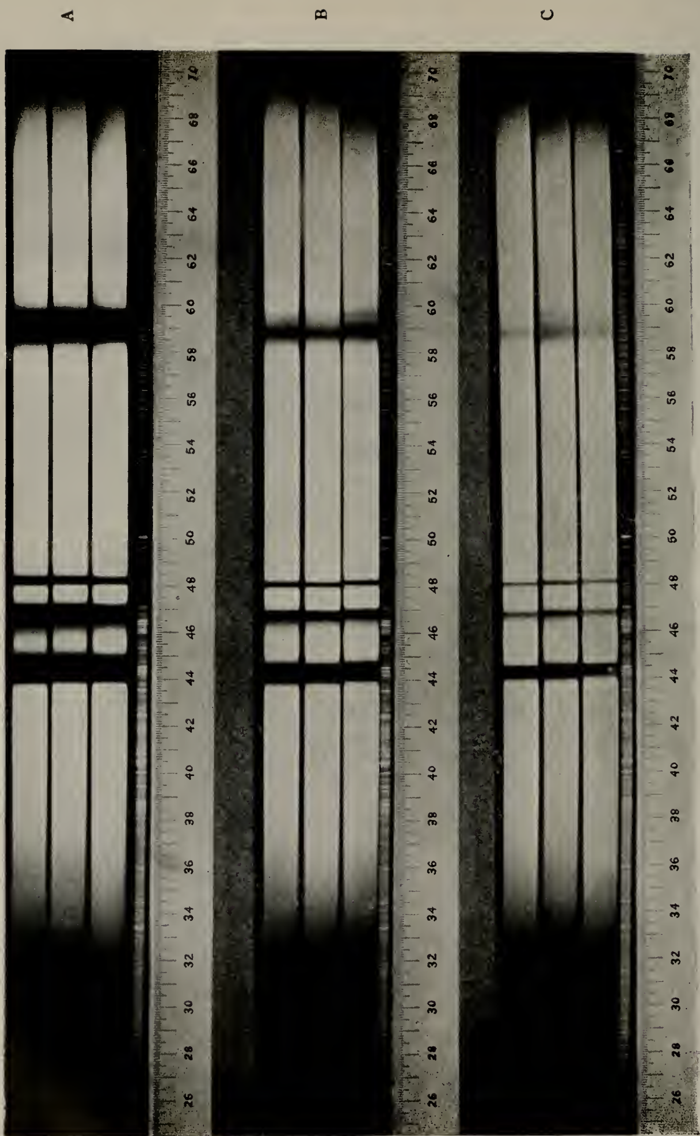


Plate XII

is the only salt of neodymium with which a change with dilution has been noted in so dilute a solution. This band narrows about 20 Å.U.

Neodymium acetate, being the salt of a weak acid, is of course less dissociated at any given concentration than a salt of a strong acid. This salt approaches complete dissociation much more slowly than the others studied. Spectrograms *A*, *B* and *C* show also that the changes caused by dilution are more marked and extend into more dilute solutions than with the chloride, bromide or nitrate. In a word, the changes in the absorption bands due to dilution seem to follow the change in dissociation, that is, they are a direct function of the number of molecules present.

Praseodymium Chloride in Water (see Plate XII)

The concentrations of solutions used in making *A*, beginning with the strip farthest removed from the numbered scale, were 2.56, 0.0256 and 0.00512 normal, the corresponding depths of absorbing layer being 0.5 cm., 50 cm. and 250 cm., respectively.

The absorption is complete in the ultraviolet up to about λ3100. The bands of praseodymium are for the most part broad and have well defined, sharp edges. The violet edge of band λ4450 is very sharp and unchanged by dilution, while the hazy red edge is hardly affected. Band λ4675 narrows towards the violet about 20 Å.U. while band λ4830 is entirely unchanged. The broad band λ5900, with slightly hazy edges, shows a total narrowing of about 25 Å.U.

The concentrations of *B* and *C*, beginning with the strips farthest from the numbered scale, are 1.28, 0.0128 and 0.00256 normal and 0.64, 0.0064 and 0.00128 normal, respectively. The corresponding depths of absorbing layer were the same as in *A*. None of the bands are affected by dilution, and we may say that Beer's Law holds very well for praseodymium chloride except for bands λ4650 and λ5900 in the most concentrated solutions. Even here the change is very slight and not to be compared with corresponding changes with dilution in salts of neodymium.

THE ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS OF CERTAIN SALTS OF NEODYMIUM AS STUDIED BY MEANS OF THE RADIOMICROMETER

The radiomicrometer is simply a thermoelement attached to a loop of thin copper wire suspended in a magnetic field. One of the greatest difficulties in constructing this element is to obtain copper wire which is free from all magnetic metals. If perfectly pure copper wire could be found an instrument could be constructed of almost any desired sensibility.

A very good specimen of small copper wire was furnished us by Leeds and Northrup, of Philadelphia. This wire was dipped in dilute nitric acid and the exterior dissolved away until the wire was of proper size. The removal of the outside coating of the wire removed practically all of the magnetic material from it, this material probably being iron from the dies through which the wire was drawn.

It was not a simple matter to construct a satisfactory thermoelectric junction. The alloys used in making this junction were ninety parts bismuth and ten parts tin and ninety-seven parts bismuth and three parts antimony. The method of making the thermoelectric junction, and of soldering it on to the ends of the loop of copper wire, we owe to Professor A. H. Pfund.[1] Fine strips of the alloys were obtained in the following manner:

A few grams of the alloy in question were fused in a vessel free from all magnetic material, and then thrown tangentially upon a clean and smooth glass plate. In this way strips of the metal were obtained of almost any desired thickness. Some were too thin to handle, those used being about 1 mm. wide, 0.01 mm. thick and about 5 mm. in length.

The thermoelement was made by soldering an end of a strip of one of the above-named alloys to an end of a strip of the other, the whole having the form of a letter V. The two free ends of the V were soldered to the two ends of the loop of copper wire. The soldered surfaces were blackened to absorb the energy more completely. At the end of the loop of copper wire opposite the thermoelement a light glass rod is fastened.

[1] Physic. Rev., **34**, 228 (1912). Physik. Z., **13**, 870 (1912).

This carries the mirror and is suspended from above by a quartz fiber. The mirror employed was about 4 square mm. This entire system, consisting of thermoelement, loop of copper wire and mirror, weighed about twenty milligrams. It was suspended by means of a quartz fiber so that the loop hung between the poles of a strong magnet. This entire system was suspended in the interior of a glass tube, the tube being closed by a ground glass stopper, and provided with suitable windows for exposing the junction and observing the mirror. The upright tube was provided with a side tube for evacuation, and by a method devised by Professor Pfund a very high vacuum could be obtained and maintained for any desired length of time. By suitably turning the ground glass stopper in the top of the glass tube, the loop of copper wire, mirror, and, indeed, the whole system could be made to occupy any position relative to the magnets, even after the entire system had been evacuated. The whole apparatus was supported upon a leveling stand and packed in cotton to protect it from external radiation, the thermal junction alone being exposed to the radiation in question.

The sensibility of the instrument used can be seen from the following data: It had a full period of 8 seconds, and with a candle at a distance of a meter gave a deflection of 15 cm., when the light was allowed to fall on the junction after passing through a glass window.

When the apparatus was pumped out and the radiomicrometer thus suspended in a vacuum the deflection for a candle at a distance of a meter was 50 cm. Since glass absorbs just about half the energy emitted by a candle, our radiomicrometer, when provided with a rock salt window and exposed to a candle at a distance of a meter, would give a deflection of about 100 cm.

How our instrument compared with the radiomicrometers constructed and used by other investigators can be seen from the following table, taken in part from the paper by Coblentz:[1]

[1] Bull. Bur. Standards, 4, No. 3.

	Whole period in seconds	Deflection in cm. per sq. mm. Candle 1 m. distance
Boys[1]	10	0.9
Paschen[2]	40	3.0
Lewis[3]	20	1.3
Coblentz[4]	40	3.6
Coblentz[4]	25	6.0
Jones and Guy	8	8.0
Jones and Guy	7	25.0 (*vacuo*)
Jones and Guy	7	50.0 (*vacuo*) rock salt window

The magnetic control due to small amounts of magnetic impurities in the copper wire was, of course, greater the more sensitive the instrument. For this reason the radiomicrometer was not used in a vacuum. The length of the quartz fiber was so chosen that a candle at a distance of a meter gave a deflection of 16 cm. The half period was 4 seconds. This sensibility was found to be quite sufficient for work in the red and infrared, and even for wave lengths as short as 4500 Å.U. The measurement could be carried out quickly and the magnetic disturbance was practically negligible.

When the thermojunction was exposed to the radiation and the source of energy removed, the instrument returned to its original zero position to within 0.5 mm. In most cases several readings were made for a given amount of radiation, and these usually agreed to within one per cent. The source of energy was a Nernst glower attached to a storage battery, the amperage being 1.2 and the voltage 110. This was found to be very constant, successive readings in the same position of the spectra agreeing well with one another.

The vessels used for holding the solutions were made of brass and gold plated. They were about 4 cm. in diameter and of the desired thickness. The ends were made of the best optical glass. Vessels of the same thickness gave practically the same deflection both when empty and when filled with water.

[1] Phil. Trans., (A) **180,** 159 (1889).
[2] Wied. Ann., **48,** 275 (1893).
[3] Astrophys. J., **2,** 1 (1895).
[4] Bull. Bur. Stand., 1 Sept. (1907).

Method of Procedure

The light from a Nernst glower was rendered parallel by a lens, then passed through the vessel containing the solution and allowed to fall on the slit of a Hilger spectroscope. The solution was first inserted into the path of the light, and then the pure solvent, this being done without disturbing the adjustment. By means of a movable framework, first the vessel containing the solution and then that containing the solvent were interposed in the path of the beam. A metal screen interposed between the Nernst glower and the vessel containing the solution allowed the light to pass through the solution only when an observation was being made. By this means the thermoelectric junction was exposed to the radiation only long enough to read the deflection of the mirror.

The light, after passing through the solution and the slit of the spectroscope, fell upon the prism of the Hilger spectroscope. A second slit was inserted in the spectroscope instead of the eye-piece. The light passed from the prism through this second slit, and was then focused on the thermal junction of the radiomicrometer.

The Hilger spectroscope contained a milled head, graduated so that the wave lengths could be read off directly. By suitably turning this head any desired wave length could be thrown upon the junction of the radiomicrometer.

The width of the slit used in the visible part of the spectrum was 0.4 mm. In the infrared where there is far more energy, the slit width was cut down to 0.22 mm. A series of readings was carried out as follows: The vessel containing the solvent was first placed in the path of the beam of light, the screen removed, and the deflection of the mirror noted. Then the vessel containing the solution was put in the same place that was formerly occupied by the vessel containing the solvent, the screen removed, and the deflection again noted. The prism was then turned slightly by means of the graduated and calibrated head, and a new wave length allowed to fall on the junction. By repeating this procedure any wave length could be allowed to fall on the junction. If we represent by

I the deflection with the solution in the path of the beam of light, and by I_0 the deflection with the solvent in the path of the light beam, the percentage of light which passed through the solution would be represented by I/I_0. In the following table we have the ratio of I/I_0 for an 0.875 normal solution of neodymium chloride, the length of the layer being 10 mm.:

λ	I/I_0	λ	I/I_0	λ	I/I_0	λ	I/I_0
4860	80	5670	1	6700	60	7720	34
4920	82	5720	0	6720	57	7760	14
4950	61	5770	1	6760	63	7810	4
4990	40	5790	3	6780	61	7860	0
5010	29	5830	11	6810	74	7920	2
5030	13	5850	23	6850	97	7980	6
5050	7	5880	42	6910	99	8020	16
5060	11	5890	63	6990	97	8060	34
5090	13	5920	79	7060	91	8110	59
5130	10	5950	90	7100	80	8180	79
5150	2	5970	92	7140	47	8230	91
5160	4	6000	95	7190	29	8330	95
5180	13	6090	94	7220	8	8360	90
5200	31	6110	92	7240	1	8400	80
5220	45	6140	93	7290	0	8450	62
5250	62	6220	91	7330	0	8500	37
5300	92	6290	94	7370	5	8550	20
5350	94	6380	98	7410	17	8605	16
5440	91	6430	98	7450	42	8660	23
5500	80	6500	99	7500	64	8720	41
5560	69	6570	99	7550	79	8780	43
5590	50	6600	95	7600	84	8890	65
5630	26	6620	91	7650	75	9000	90
5650	9	6660	75	7690	57	9580	100

The above table may be taken as typical of the results obtained with any given salt. When we first began to investigate any given salt we made a preliminary survey of its spectrum, noting the approximate positions of the absorption lines and bands. We then made our observations very close together over the regions in which the preliminary survey had indicated the presence of lines and bands. The number of absorption lines and bands, as is well known, is very great in the case of neodymium compounds, and these lines and bands frequently have very sharp edges. This made the work with

this substance very difficult. The proper width of slit and position had to be chosen or a considerable error would result. Given a slit width which was approximately the same as that of an absorption line, a very slight movement of the slit or prism would change very greatly the total amount of energy falling on the thermal junction.

Take the neodymium band $\lambda 4275$, which is very intense but narrow. On both sides of this band there is a region of almost perfect transparency. If the slit width necessary to give the desired deflection was greater than the width of this band, light would pass through around the edges of the band, and an error, which might be of very considerable magnitude, would result. With substances which did not contain such fine lines and bands the work would be much simpler.

The entire spectrum from wave lengths $\lambda 4000$ to $\lambda 20000$ was observed at intervals of from 20 Å.U. to 50 Å.U, except in the regions where the preliminary survey indicated the absence of absorption lines and bands.

An examination of the preceding table will show at $\lambda 4820$ a transparency of 80 per cent., which rapidly decreases, reaching the first minimum at $\lambda 5050$. There the transparency amounts to only 7 per cent. The transparency then increases a little and quickly drops to 2 per cent. at $\lambda 5150$. The transparency then increases, becoming nearly complete at $\lambda 5350$. We have here, then, a double band with greater absorption on the red side. Other minima appear at $\lambda 5720$, $\lambda 7300$, $\lambda 7860$ and $\lambda 8605$. Bands $\lambda 7300$, $\lambda 7860$ and $\lambda 8605$ do not appear on the photographic plate, and the last two seem never to have been detected before.

The salts of neodymium were studied as far as $\lambda 20000$, but beyond 1μ there seems to be complete transparency. The absorption of water is, as is well known, very great in the region $\lambda 12000$ to $\lambda 20000$.

Discussion of the Results

The results are plotted in the following eleven curves. The abscissae are percentage transparencies, the ordinates are wave lengths. These curves, since they represent the transparen-

cies of the solutions in question, are called *transmission curves.*

Figs. 1, 2 and 3 represent the transparency of solutions of

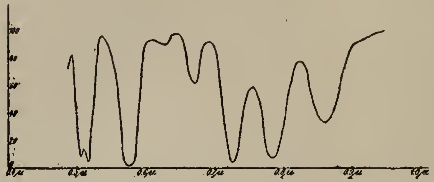


Fig. 1

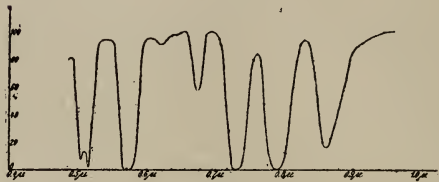


Fig. 2

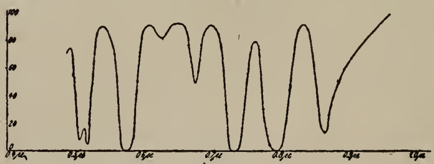


Fig. 3

neodymium chloride expressed in terms of Beer's Law. If we represent the concentration by N and the depth of layer by d,

$$Nd = constant$$

The concentration represented in Fig. 1[1] is 3.43 normal, in Fig. 2 0.875 normal, and in Fig. 3 0.472 normal. The depth of layer represented by Fig. 1 is 2.5 mm., by Fig. 2 10 mm., and by Fig. 3 20 mm. The concentration and depth of layer were thus varied so as to keep Nd constant.

[1] Our attention was drawn to the existence of these bands in the infrared by Pfund, who had already mapped them radiometrically for neodymium nitrate.

If the solvent plays no rôle in the absorption, the three sets of curves must fall directly over one another, i. e., be identical, since the number of absorbing parts in the path of the beam of light is kept constant. A comparison of the curve shows that, in general, the more concentrated the solution the less the transparency and the broader the absorption bands. In the more dilute solution the intensity of the bands is greater. This comes out very clearly in the red and infrared region, where there is greater accuracy of measurement.

Take the three absorption bands, $\lambda 7300$, $\lambda 7850$ and $\lambda 8600$. In Curve 1 the minima of these bands are approximately 4, 8, and 33 per cent., while the minima in Curve 2 are much less. In Fig. 2 the bands $\lambda 7300$ and $\lambda 7850$ reach the abscissa, which means that there is no transmission. At this dilution the band $\lambda 8600$ has still considerable transparency, as will be seen by the fact that it remains a considerable distance above the abscissa. The band $\lambda 8600$ does not reach the abscissa even at the dilution represented in Fig. 3.

All of the bands manifest the above phenomena, the change in intensity being greatest where the change in dilution is greatest, i. e., from Curve 1 to Curve 2. With increase in dilution the position of the middle of the band is displaced toward the region of greater wave length.

Similar results were obtained with neodymium bromide, and these are plotted in Curves 4, 5 and 6. The concentrations and depths of layer were varied so that the product of the two remained constant. The work with the bromide was, therefore, done in terms of Beer's Law. The concentrations used were 1.66 normal, 0.415 normal and 0.207 normal, the corresponding depths of the solution being 2.5 mm., 10 mm. and 20 mm. We find here the same general changes in the intensities of the bands as with the chloride. The more dilute the solution the more intense and the narrower the band.

This is shown by comparing Figs. 4, 5 and 6. In Fig. 4, which represents the most concentrated solution of the three, the bands are the least intense. In Fig. 5 the opacity of two of the

bands has become complete, shown by the fact that these touch the abscissa.

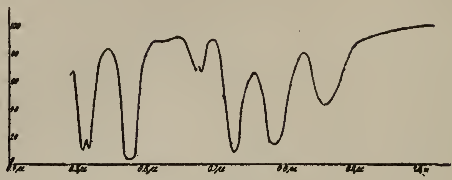


Fig. 4.

Fig. 5.

Fig. 6

Neodymium nitrate was also studied and the results are plotted in Curves 7, 8 and 9. The concentrations used were 2.95, 0.736 and 0.368 normal. The depths of layer were 2.5 mm., 10 mm. and 20 mm.

Band λ5700, Curve 7, appears to be an exception to the general relation pointed out above, connecting intensity and width of band with dilution. This was the first band studied by means of the radiomicrometer, and comparatively small deflections were observed in this region of the spectrum. The

remaining bands of neodymium nitrate, however, show the same relations that have been pointed out for the chloride and bromide; with increasing dilution the intensities of the

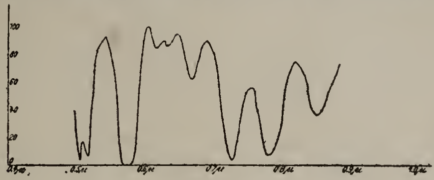


Fig. 7

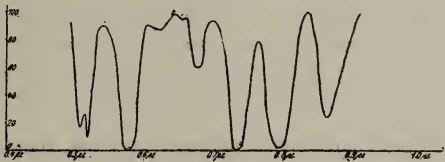


Fig. 8

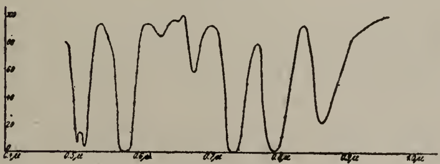


Fig. 9

bands increase and the centers seem to be displaced somewhat towards the longer wave lengths.

We then have three salts, neodymium chloride, neodymium bromide and neodymium nitrate, all of which show a marked increase in the intensity of the absorption bands with increase in dilution, when the product of concentration and depth of layer is kept constant, i. e., when the conditions demanded by Beer's law are fulfilled.

Possible Explanation

It is well known that a resonator vibrates more strongly if

excited by the vibrations for one single vibrating resonator of the same pitch than when set into vibration by a large number of resonators, one of which has the same period as its own, and the others slightly different periods. In other words, if several vibrators are near one another, every one exerts a certain influence on its neighbors. The result is that no one of them has exactly the same period as the original resonator.

The presence of one vibrator seems to exercise a damping influence on the other, and causes it to vibrate with a period slightly different from its normal period. We thus have less perfect resonance.

The absorption of light by solutions appears to be a resonance phenomenon. In a concentrated solution the vibrators are relatively close to one another and mutually affect one another. The result is an imperfect resonance, and, consequently, the absorption bands are less intense in the more concentrated solution.

The vibrators are farther removed from one another in the more dilute solutions, and in most cases are probably surrounded by large amounts of water of hydration. The damping effect would not be so pronounced, and a resonator would have greater freedom to vibrate in its own period. In such cases we would have a more nearly perfect resonance, and the resulting absorption bands would be more intense. This tentative explanation seems to account for the observed facts. Fig. 10 is plotted from the results for neodymium sulphate, and Fig. 11 from those for neodymium acetate. The concentration of the sulphate is 0.118 normal, and of the acetate 0.84 normal. The length of the solution of the sulphate is 10 mm. and of the acetate 2.5 mm.

The absorption of the acetate, for a given concentration, is much greater than that of any other neodymium salt thus far studied. This agrees with the results obtained photographically.

The absorption of water beyond 1μ is very great, as has already been stated. If we are working with very concentrated solutions and use a "water" vessel of the same thickness as the "solution" vessel, it is obvious that the results would

not be comparable. Take the 3.43 normal solution of neodymium chloride, it contains, for a given thickness, only about ninety per cent. as much water as the same thickness of pure water. It is then obvious that in the longer wave lengths

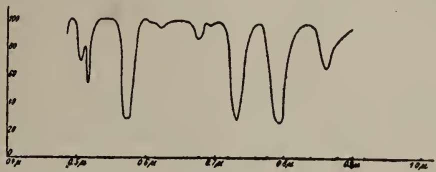


Fig. 10

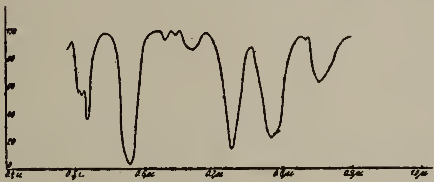


Fig. 11

a correction term must be introduced for this difference. This was practically negligible with salts of neodymium, since these do not seem to have any bands in the region where water has appreciable absorption.

Salts of praseodymium have bands in the infrared, at least as far as 2μ. In such cases the above correction must be introduced. This correction can be introduced in either of two ways. We can take the specific gravity of the solution and from the concentration calculate the amount of water present. We can then use a "water" vessel of suitable thickness. For example, if the very concentrated solution in question contains only 90 per cent. of water, and we use a vessel for the solution which is 10 mm. thick, we must use a vessel for the water which is only 9 mm. thick. In this way the beam of light is made to pass through the same amount of water both in the case of the solution and of the solvent, and the absorption due to water is, therefore, the same in the two cases.

The second method of procedure is to allow the "water" vessel and the "solution" vessel to be of the same thickness, and to apply mathematically the proper correction to the results obtained.

SUMMARY AND GENERAL DISCUSSION OF MOST IMPORTANT RESULTS

Although in the discussion of each plate, there has been given a brief account of the changes and points of special interest, it is thought wise to bring together the most important facts established, and, if possible, try to interpret them. In the study of the effect of high temperatures on aqueous solutions, it is seen that while certain bands change in intensity, becoming broad or in certain instances actually shifting their positions, yet, other bands are apparently unchanged over a range of 200°.

Plates I, II, III and IV, which are the absorption spectra of neodymium chloride, bromide, nitrate and acetate, respectively, show marked change with rise in temperature in only the two bands $\lambda 5275$ and $\lambda 5800$. There is a general tendency for almost all the other bands to become slightly more diffuse, although it is difficult to say that this may not be caused by general absorption. However, with bands $\lambda 4275$ and $\lambda 5800$ the change is a real one. Experiments made by overexposing the strips corresponding to the high temperatures had little or no effect on the changes produced by raising the temperature. Since the development of a photographic plate depends upon the amount of light falling upon it, independent of the period of time it is falling, it is clear that the effect of general absorption could be counterbalanced by increased time of exposure.

The two bands mentioned above widened rapidly as the temperature was raised, this widening being, in both cases, almost entirely towards the longer wave lengths.

The band $\lambda 5800$, in the most concentrated solutions, widened as much as 80 Å.U., while the amount of widening was directly dependent upon the concentration. It is always greater

between the second and third strips. This is what we should expect, since the change in dilution between the two solutions whose spectrogram they represent is one hundred times, while the succeeding dilution was only five times. The violet edge of this band remains almost constant over the range of temperature studied.

The band $\lambda 4275$, a very sharp, intense band at the lower temperatures, becomes rapidly diffuse as the temperature of any solution is raised. With this band, as with the $\lambda 5800$ band just discussed, the change is taking place almost exclusively on the red edge, the shading being a gradual one. This edge, the definition of which at ordinary temperature could be seen almost to 1 Å.U., covers about 40 Å.U. at 190°. The double band with its center near $\lambda 5150$ remains about constant in any given section, but in those bands whose width or intensity is changed by change in temperature the change is greatest in the most concentrated solutions, i. e., where the number of molecules is greatest.

Salts of praseodymium are only slightly affected by change in temperature. In the most concentrated solutions all the bands are slightly widened, while in the more dilute solutions there is no appreciable change.

In the salts of uranyl studied, it was found that nearly every band widened with rise in temperature, the widening in two instances being rapidly towards the red. Several of the bands seem to have their centers shifted as much as 15 Å.U. towards the red end of the spectrum.

As mentioned in the discussion of the plates, the uranyl bands almost all occur in the ultraviolet end of the spectrum, and in this region the general absorption increases rapidly as temperature rises. On account of this, together with the haziness of all uranyl bands, it is difficult to make exact measurements upon them. It seems evident that in some cases both the width and position of the bands are changed by change in temperature. The change is always a widening of the band in question as the temperature rises.

In the part of this paper which deals with the effect of high dilution, it has been shown that at least three of the neodymium

bands are affected, namely, $\lambda 4275$, $\lambda 5150$ and $\lambda 5800$. Of these three the change is apparently greatest in $\lambda 5800$, next in $\lambda 5150$, and least in $\lambda 4275$. It cannot be said to be really least in $\lambda 4275$ but rather less noticeable. It is probable that the percentage change, with regard to the total width of the band, is much greater with this band than in the two preceding bands.

The change in $\lambda 5800$ is a widening of about 60 Å.U. in the most concentrated solutions, as we pass in the direction of the concentrated solutions. This widening, as in the temperature effect, is entirely towards the red end of the spectrum. The widening of the double band near $\lambda 5150$ is uniform towards both ends of the spectrum. This change is appreciable only in the very concentrated solutions.

Considering a single plate, which represents the spectrogram of three different dilutions, in terms of Beer's Law we see the following:

This change is greatest in Section *A*, i. e., the most concentrated solution; less in *B*; and hardly measurable in *C*.

The change is greater with the acetate than with the other salts of neodymium, and is always greatest where the difference in concentration is greatest, i. e., between Strips 2 and 3.

When we consider the effect of dilution on the dissociation we see it is in this same ratio, i. e., there is a much greater percentage change in the relative number of molecules present in concentrated than in dilute solutions, for a given change in dilution.

In that dilution of any solution where the relative number of molecules is greatest—the association greatest—bands $\lambda 4275$, $\lambda 5150$ and $\lambda 5800$ are widest, and the change in dilution which affects the relative number of molecules to the greatest extent causes the greatest change in the bands. In the more dilute solutions where this change in the number of molecules is small, there is a relatively small change in the width or intensity of the bands.

A rise in temperature produces the same change upon bands $\lambda 4275$ and $\lambda 5800$ as concentrating the solution, that is, rise in temperature and dilution produce the reverse effect. Band

$\lambda 5100$ is changed by dilution and not by temperature. From these facts it seems that band $\lambda 5100$ may be associated with the molecules themselves, while bands $\lambda 4175$ and $\lambda 5800$ have more to do with the hydrated molecule. A rise in temperature would make the hydrated absorbers, or the hydrated system containing the absorbers, simpler, and, therefore, probably freer to respond in resonance to a larger number of wave lengths. This would cause a widening of the absorption bands. Concentrating the solution, i. e., decreasing the actual amount of solvent, would, according to the mass law, decrease the amount of solution, and, hence, have the same effect as raising the temperature. This is exactly what is shown to be the case by the plates with bands $\lambda 4275$ and $\lambda 5800$.

The $\lambda 5100$ band is not appreciably affected by temperature, but is changed by dilution, being widest in the most concentrated solutions.

Since temperature has little or no effect on this band, it is probable that here hydration plays very little part. Since the band widens as the number of molecules is increased, it seems to be in some way associated with the unhydrated molecules.

So far as can be seen from the photographic plates, the other neodymium bands are affected neither by dilution nor by temperature. The absorbers in this case are probably associated with the neodymium atoms or ions.

DESCRIPTION OF PLATES

Plate I. *A*. Neodymium Chloride in Aqueous Solution. Concentration, saturated. Depth of layer, 1 cm. Respective temperatures, 20°, 45°, 70°, 95°, 115°, 140° and 165°, with lowest temperatures nearest spark lines. Exposures made on rising temperature.

B. The same solution used in Plate *A*, with exposures made as cell cooled. Depth of layer and concentration the same as Plate *A*. Temperatures, 165°, 140°, 115°, 95°, 70°, respectively. Highest temperatures nearest spark lines.

Plate II. *A*. Neodymium Bromide in Aqueous Solution. Concentration, 1.66 normal. Depth of cell, 1 cm. Respective temperatures, 20°, 45°, 70°, 95°, 120°, 140°, 175°, 190°. Lowest temperature nea est spark spectra.

B. Neodymium Bromide in Aqueous Solution. Concentration, 0.166 normal. Depth of cell, 10 cm. Respective temperatures, 20°, 45°, 70°, 95°, 115°, 135°, 155° and 190°. Highest temperature nearest spark spectra.

Plate III. *A*. Neodymium Nitrate in Aqueous Solution. Concentration, 0.1 saturated. Depth of layer, 10 cm. Temperatures, 20°, 45°, 70°, 95°, 115°, 140°, 165°, 190°. Exposures made as temperature was raised. Lowest temperature nearest spark lines.

B. The same solution of neodymium nitrate as used in Plate *A*. Concentration and depth of layer identical with *A*. Temperatures, 190°, 165°, 140°, 115°, 95°, 70°, 45° and 20°. Exposures made on falling temperatures. Highest temperature nearest spark lines.

Plate IV. *A*. Neodymium Acetate in Water. Concentration, 0.1 saturated. Depth of cell, 10 cm. Trace of acetic acid added to prevent precipitation. Temperatures, 20°, 45°, 70°, 95°, 120°, 140°, 160° and 190°. Exposures made on rising temperature. Lowest temperature nearest spark line.

B. Solution, depth of cell and concentration the same as *A*. Temperatures, 190°, 165°, 145°, 125°, 100°, 75°, 50° and 25°. Exposures made on falling temperatures.

Plate V. *A*. Praseodymium Nitrate in Water. Concentration, 2.6 normal. Cell depth, 1 cm. Temperatures, 12°, 32°, 52°, 72°, 92°, 112°, 125° and 145°. Lowest temperature nearest spark lines.

B. Praseodymium Nitrate in Water. Concentration, 0.26 normal. Cell depth, 10 cm. Temperatures, 20°, 45°, 70°, 95°, 115°, 135° and 165°. Lowest temperature nearest spark lines.

Plate VI. *A*. Uranyl Nitrate in Water. Concentration, 0.2 normal. Cell depth, 1 cm. Temperatures, starting with strip nearest spark lines, were 20°, 40°, 60°, 80°, 100° and 120°, respectively.

B. Uranyl Nitrate in Water. Concentration, 0.02 normal. Depth of cell, 10 cm. Temperatures, starting with exposure nearest spark lines, were 20°, 45°, 70°, 95°, 115°, 140° and 165°, respectively.

Plate VII. *A*. Uranyl Sulphate in Water. Concentration 0.166 normal. Depth of cell, 1 cm. Temperatures, beginning nearest spark lines, 20°, 45°, 70°, 95°, 115°, 135°, 155° and 185°, respectively.

B. Uranyl Sulphate in Water. Concentration, 0.2 normal. Cell depth, 10 cm. Respective temperatures, beginning nearest spark lines, were 20°, 45°, 70°, 95°, 115°, 140° and 165°.

Plate VIII. *A*. Neodymium Chloride in Water. Concentrations, 2.05, 0.0205 and 0.00401 normal. Respective depths of cell, 0.5 cm., 50 cm. and 250 cm. Most dilute solution nearest spark lines.

B. Neodymium Chloride in Water. Concentrations, 1.025, 0.01025 and 0.00205 normal. Depths of cell, starting with strip farthest from spark lines, were 0.5 cm., 50 cm. and 250 cm., respectively.

C. Neodymium Chloride in Water. Concentrations, 0.512, 0.00512 and 0.00102 normal. Depths of cell, beginning with strip farthest removed from spark lines, were 0.5 cm., 50 cm. and 250 cm., respectively.

Plate IX. *A*. Neodymium Bromide in Water. Concentrations, 1.66, 0.0166 and 0.0033 normal. Corresponding depths of cell, 0.5 cm., 50 cm. and 250 cm., respectively. Most dilute solution nearest spark lines.

B. Neodymium Bromide in Water. Concentrations, 0.83, 0.0083 and 0.00166 normal. Corresponding depths of cell, 0.5 cm., 50 cm. and 250 cm., respectively. Most dilute solution nearest spark lines.

C. Neodymium Bromide in Water. Concentrations, 0.415, 0.00415 and 0.000803 normal. Corresponding depths of cell, 0.5 cm., 50 cm. and 250 cm., respectively.

Plate X. *A*. Neodymium Nitrate in Water. Concentrations, 2.15, 0.0215 and 0.00430 normal, respectively. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively. Most dilute solutions nearest spark lines.

B. Neodymium Nitrate in Water. Concentrations, 1.075, 0.01075 and 0.00215 normal. Corresponding cell depths were 0.5 cm., 50 cm. and 250 cm., respectively.

C. Neodymium Nitrate in Water. Concentrations, 0.537, 0.00537 and 0.00107. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively. Most dilute solutions nearest spark lines.

Plate XI. *A*. Neodymium Acetate in Water. Concentrations, saturated, 0.01*s* and 0.002*s*, where *s* represents a saturated solution of the salt in water at 25°. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively.

B. Neodymium Acetate in Water. Concentrations, 0.25*s*, 0.005*s* and 0.001*s* (*s* being a saturated solution as above). Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm.

C. Neodymium Acetate in Water. Concentrations, 0.25*s*, 0.0025*s* and 0.0005*s*. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively.

Plate XII. *A*. Praseodymium Chloride in Water. Concentrations, 2.56, 0.0256 and 0.00512 normal, respectively. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm.

B. Praseodymium Chloride in Water. Concentrations, 1.28, 0.0128 and 0.00256 normal. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively.

C. Praseodymium Chloride in Water. Concentrations, 0.64, 0.0064 and 0.00128 normal. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively.

[Contributions from the Chemical Laboratory of Harvard College]

IODTRIBROMNITROBENZENE

By C. Loring Jackson and Webster N. Jones

The 2,4,6-tribrom-3-nitraniline, which formed the starting point of this research, melts according to Körner[1] at 102°.5, according to Remmers[2] at 214°–215°; it was obvious, therefore, that a study of this substance was necessary before we could begin the work which we had undertaken. Körner prepared his product by the action of bromine vapor on *m*-nitraniline, and on repeating his work we obtained exactly the same results (except that our product melted at 101°.5 instead of 102°.5 as given by Körner), and in this we agree with Nölting and Collins[3] and Bentley[4], who also repeated Körner's work. Bentley also tried to follow the method of Remmers, the action of nitric acid on tribromacetanilide, but did not succeed in finding the conditions for the formation of the tribromnitracetanilide, obtaining instead tetrabrombenzene, dinitrodibrommethane, bromanil, oxalic acid and picric acid. After some trouble we found the conditions under which the tribromacetanilide was converted into tribromnitracetanilide, which consisted in heating on the steam bath until the first brown fumes appeared, that is, for less than a minute. Longer action gave a mixture similar to that described by Bentley, from which we isolated bromanil, and un-

[1] Gazz. chim. ital., **1874**, 348.
[2] Ber. d. chem. Ges., **7**, 351 (1874).
[3] Z. Chem., **1875**, 347.
[4] This Journal, **20**, 472 (1898).

doubtedly should have detected his other products if we had studied this reaction as carefully as he did, but it lay outside of the limits of our research. The 2,4,6-tribrom-3-nitracetanilide melts at 208°–209°. Remmers does not mention his melting point. When boiled for 5 hours with sulphuric acid of specific gravity 1.44, this substance was converted into Körner's tribromnitraniline melting at 101°.5. Remmers' tribromnitraniline melting at 214°–215°, therefore, does not exist. He found great difficulty in saponifying his acetanilide, neither sodic hydroxide nor hydrochloric acid producing any effect upon it; finally he thought he had achieved the desired result by heating in a sealed tube with aqueous ammonic hydroxide. This and the higher melting point suggest that his substance may have been the unaltered acetanilide, and that he was misled by a bad analysis.

The 2,4,6-tribrom-3-nitrodiacetanilide of Remmers melts at 168°–169°, and is evidently the substance with this melting point described by H. L. Wheeler[1] as the monacetanilide. This latter substance ($C_6HBr_3NO_2NHC_2H_3O$) melts at 208°–209°, as already stated.

The 1-iod-2,4,6-tribrom-3-nitrobenzene melts at 144°–145°; it reacts at ordinary temperatures with an alcoholic solution of sodic ethylate, giving a mixture of the bromide, iodide and nitrite of sodium and organic products, from which we isolated an ioddibromnitrophenetole melting at 121°. The other compounds, which must have been formed, appeared in such an oily state that we were unable to obtain any of them pure in the time at our disposal.

The substances 2,4,6-tribrom-3-nitraniline, 2,4,6-tribrom-3-nitrobenzene, 2,4,6-tribrom-1-iod-3-nitrobenzene and 2,4,6-tribrom-1,3-dinitrobenzene seemed well adapted for the study of the effects of different radicals on the ease with which the bromine can be replaced, and we had even intended to make quantitative studies of the progress of such replacements, but we were obliged to abandon this plan as far as the nitraniline was concerned, because its rate of action was so much slower than those of any of the other substances, and

[1] This Journal, **17**, 702 (1895).

also because the amorphous unmanageable products of its reactions with alcoholates indicated that they were not the simple formation of alkyl ethers, which had been proved to take place with the other compounds. The results of our preliminary experiments with sodic alcoholates show the expected retarding action of the amino group and the accelerating effect of the iodine, which, however, seems to be less active than the nitro group.[1] In all our experiments sodic methylate entered into reaction much more sluggishly than sodic ethylate.

The one really definite result of our work in this line was the great inertness of all of these compounds, except the tribromdinitrobenzene, toward aniline, the amount of reaction being trifling after long heating at 100° or even at the boiling point of aniline.[2] This shows that the amino group, hydrogen, or iodine, exercises much less loosening effect on the bromine than a second nitro group in the same position, since tribromdinitrobenzene is converted into trianilinodinitrobenzene[3] by short heating. A third nitro group (in 2,4,6-tribrom-1,3,5-trinitrobenzene) produces the complete replacement of the bromine in the cold, whereas the dinitro body does not react until heated.

EXPERIMENTAL

Preparation of 2,4,6-Tribrom-3-nitraniline according to Körner[4]

As Körner does not give very full directions for this process, we describe our work in detail. Ten grams of *m*-nitraniline were dissolved in a liter of strong hydrochloric acid and diluted up to 7 liters. A stream of air saturated with bromine vapor was then drawn through this solution, until an excess was indicated by the change of the color of the liquid from yellow to light red. The tribromnitraniline, which began to separate toward the end of the process, was washed with water, then with dilute ammonic hydroxide, and finally again with water, after which it was purified by crystallization from alco-

[1] Compare This Journal, **13**, 164 (1891); **14**, 363 (1891).
[2] *Ibid.*, **14**, 363 (1891).
[3] *Ibid.*, **11**, 448 (1889).
[4] Gazz. chim. ital., **1874**, 348.

hol, until it showed the melting point 101°.5. Körner gives 102°.5, but we have never succeeded in raising it above the temperature given by us. Our thermometer was found to register 100° in steam.

0.2201 gram substance gave 0.3315 gram AgBr.

	Calculated for $C_6HBr_3NO_2NH_2$	Found
Br	63.97	64.07

Study of the Method of Remmers[1] for Preparing 2,4,6-Tribrom-3-nitraniline

Tribromacetanilide was made by boiling under a reverse condenser for 2 hours a mixture of tribromaniline, acetyl chloride and glacial acetic acid. The product crystallized in long, white needles and melted at 232°. Remmers gives the same melting point for this substance.

Ten grams of this tribromacetanilide dissolved in 50 cc. of fuming nitric acid (specific gravity 1.50) were heated on the steam bath until the first brown fumes appeared, which happened from 45 seconds to one minute after the heating began. The product was then diluted with water, when a sharp odor was noticed, probably the dibromdinitromethane observed by Bentley.[2] The precipitate was semisolid and yellow at first, but turned reddish brown on exposure to the air. After the mass had stood for 2 weeks it was crystallized at first from alcohol, and then from benzene, until it showed the constant melting point 208°–209°. Remmers does not give the melting point of this substance.

Half a gram of the compound was heated under a return condenser for 5 hours with 30 cc. of sulphuric acid of specific gravity 1.44, when the solid turned from white to yellow, and after crystallization from alcohol showed the constant melting point 101°.5, and crystallized in star-shaped clusters of needles, so there can be no doubt that it is identical with the tribromnitraniline obtained according to Körner.

2,4,6-Tribrom-3-nitrodiacetanilide, $C_6HBr_3NO_2N(C_2H_3O)_2$.—Fifteen grams of tribromnitraniline dissolved in 30 grams of

[1] Ber. d. chem. Ges., **7**, 351 (1874).
[2] This Journal, **20**, 472 (1898).

glacial acetic acid were boiled under a return condenser for 2 hours with 30 grams of acetyl chloride and a little anhydrous sodic acetate. The white product was crystallized from alcohol until it showed the constant melting point 168°–169°. It is evidently therefore the substance melting at 169° obtained by H. L. Wheeler[1] in the same way, and supposed by him to be the monacetanilide. Remmers,[2] who had prepared it previously, recognized it as the diacetanilide, but gave no melting point.

0.2110 gram substance gave 0.2604 gram AgBr.

	Calculated for $C_6HBr_3NO_2N(COCH_3)_2$	Found
Br	52.25	52.53

Properties of 2,4,6-Tribrom-3-nitrodiacetanilide.—White octahedra, or dodecahedra, which melt at 168°–169°. It is soluble in acetone, slightly soluble in cold chloroform, benzene, or glacial acetic acid, more soluble in these liquids when hot; very slightly soluble in cold alcohol, or methyl alcohol, more soluble hot; almost insoluble in cold ligroin, slightly soluble in hot; essentially insoluble in water whether cold or hot. The best solvent for it is alcohol or acetone. Hot sodic hydroxide solution converts it into the monacetanilide.

2,4,6-Tribrom-3-nitracetanilide, $C_6HBr_3NO_2NHCOCH_3$.—This substance could be made by treating the tribromnitranilide with a little more than the calculated amount of acetyl chloride in glacial acetic acid, but we found it more convenient to prepare the diacetanilide as already described, and then remove one of the acetyl groups with sodic hydroxide. Ten grams of tribromnitrodiacetanilide were heated with a solution of sodic hydroxide (5 grams in 100 cc.), and, as the liquid became warm, the diacetanilide went into solution. After it had been boiled for 15 minutes, hydrochloric acid was added, which threw down a white precipitate, and this was purified by crystallization from alcohol until it showed the constant melting point 208°–209°. This substance was made

[1] This Journal, **17**, 702.
[2] Ber. d. chem. Ges., **7**, 351 (1874).

by Remmers[1] by the action of nitric acid on tribromacetanilide, but he gave no melting point.

0.1748 gram substance gave 0.2366 gram AgBr.

	Calculated for $C_6HBr_3NO_2NHC_2H_3O$	Found
Br	57.55	57.59

Properties of Tribromnitracetanilide.—It forms white, rhombic crystals from alcohol, methyl alcohol, or glacial acetic acid, needles from benzene. It melts at 208°–209°. It is soluble in cold glacial acetic acid, more so in hot; slightly soluble in cold alcohol, or acetone, more soluble in hot; practically insoluble in cold ether, slightly soluble in hot; essentially insoluble in water, or ligroin, hot or cold. It is distinctly less soluble than the diacetanilide. The best solvent for it is alcohol or acetone. Heating with sodic hydroxide for 15 minutes or more does not remove the acetyl group. The action of nitric acid upon it was studied under many different conditions. The principal product was bromanil, identified by its color and crystalline form.

The behavior of 2,4,6-tribrom-3-nitraniline was studied with various reagents, and, although no new substances were isolated, a brief account of our results seems to us worth while. Aniline, when warmed with the tribromnitraniline on the steam bath for 6 hours, had little or no effect, as the original substance was recovered unaltered. After 6 hours at the boiling point of aniline a blue-black substance, probably aniline black, was formed, but apparently in no great amount, as in this case also we succeeded in recovering the greater part of the original substance.

Sodic ethylate or methylate did not act on the tribromnitraniline at ordinary temperatures, since no test for bromide was obtained, after the compounds had stood together for 2 or even 5 months. When the mixture was heated, sodic ethylate produced no sodic bromide below 70°, and even at this temperature it was necessary to heat for 3 hours to obtain a faint test, which was hardly increased by 2 hours more, but, when the temperature was raised to 80°, a strong test was ob-

[1] Ber. d. chem. Ges., **7**, 351 (1874).

tained in half an hour. Sodic methylate acted much more slowly, as heating it with the tribromnitraniline to 100° gave no action in half an hour, and a strong test for bromide was not obtained till after $2^1/_4$ hours. Even after 4 hours much unaltered substance was recovered, and the original compound did not begin to disappear till after 8 hours. 2,4,6-Tribrom-3-nitrobenzene gave a strong test for bromide after half an hour, when exposed to the same conditions.

As the tribromnitracetanilide is very stable toward sodic hydroxide, we tried the action of sodic alcoholates upon it in the hope that the acetyl group might diminish the retarding effect of the amino group enough to bring about a reaction with the bromine, before the amino compound was formed. With sodic methylate tests were made at measured intervals, and it was found that a faint indication of bromide appeared only after $2^1/_4$ hours on the steam bath, and that it did not become strong until the mixture had been heated more than $5^3/_4$ hours; as the tribromnitraniline gave a strong test in $2^1/_4$ hours, the acetanilide acted more slowly than the free amine. Sodic ethylate gave a strong test after 4 hours on the steam bath (it was not tested earlier), so its action here also is distinctly more vigorous than that of the methylate. No test for nitrite was obtained in any of these experiments. The organic products of these reactions were reddish brown and amorphous; they did not melt below 280°, and were but slightly soluble in all the organic solvents. We did not succeed in bringing them into a state fit for analysis.

1-Iod-2,4,6-tribrom-3-nitrobenzene, $C_6HIBr_3NO_2$.—Ten grams of tribromnitraniline were dissolved in 150 cc. of glacial acetic acid and mixed with 50 cc. of sulphuric acid diluted with an equal volume of water. The mixture was cooled with ice, and shaken for some time so that only small crystals of the aniline should form, since large ones would have resisted the diazotization. To the cold mixture 2.5 grams of sodic nitrite dissolved in 10 cc. of water were added in small portions at a time with thorough shaking, the addition taking half an hour. As the diazo reaction took place, the semisolid mass changed from yellow to white and in order to

be certain that it was complete, the mixture was allowed to stand in the cooling bath for 2 hours; at the end of this time an ice-cold solution of 12 grams of potassic iodide was added gradually with thorough shaking, which took half an hour, during which time the mixture turned from white to very dark gray. After it had stood overnight, it was heated on the steam bath for three-quarters of an hour to form the iodtribromnitrobenzene, the reaction being accompanied by a change of color from gray to yellow. The liquid was then cooled with ice to separate out as much of the iod compound as possible, and the solid was freed from iodine by washing it successively with a concentrated solution of potassic iodide, a solution of sodic thiosulphate, and finally with water. The yellowish white residue was then crystallized from alcohol until it was perfectly white and showed the constant melting point 144°–145°. The average yield of the crude product was 52 per cent. of the theoretical.

0.2089 gram substance gave 0.3439 gram AgBr + AgI.

	Calculated for $C_6HBr_3INO_2$	Found
$Br_3 + I$	75.53	75.61

Properties of 1-Iod-2,4,6-tribrom-3-nitrobenzene.—It crystallizes from alcohol in white, rectangular plates which melt at 144°–145°. It is very soluble in chloroform; soluble in cold benzene, very soluble in hot; fairly soluble in cold, more soluble in hot ether; slightly soluble in cold alcohol, or glacial acetic acid, more soluble in hot; essentially insoluble in water or ligroin, whether cold or hot. Alcohol is the best solvent for it.

Action of Sodic Ethylate on 1-Iod-2,4,6-tribrom-3-nitrobenzene. Ioddibromnitrophenetole, $C_6HIBr_2OC_2H_5NO_2$.—Twenty grams of iodtribromnitrobenzene dissolved in 100 cc. of dry benzene were mixed with a solution of sodic ethylate made by treating 3.75 grams of sodium with 100 cc. of absolute alcohol. There were therefore 4 molecules of ethylate for each molecule of the substituted benzene. The mixture was allowed to stand at ordinary temperatures for 10 days,

when it was found that a precipitate had formed, which was soluble in water, and gave tests for bromide, iodide, and nitrite. The filtrate from this precipitate was allowed to evaporate spontaneously, and, by pouring off the mother liquor at sufficient intervals, was divided into three portions, the first of which was a yellow, crystalline solid, the second a reddish, and the third a red oil. The crystalline portion was washed thoroughly with water and then recrystallized from alcohol, when after 8 crystallizations it showed the constant melting point 121°.

I. 0.1951 gram substance gave 0.2639 gram AgBr + AgI.
II. 0.1558 gram substance gave 0.2103 gram AgBr + AgI.

	Calculated for $C_6HIBr_2OC_2H_5NO_2$	Found I	Found II
2Br + I	63.63	63.56	63.42

The specimens used in the analyses came from two different preparations. The determination of the constitution of the substance must be left for future experiment.

Properties of Ioddibromnitrophenetole.—It crystallizes from alcohol in long, white, rectangular prisms, which turn slightly brown on standing. Melting point, 121°. It is very soluble in ether, chloroform, or glacial acetic acid; tolerably soluble in cold methyl alcohol or ligroin, more soluble in hot ligroin; slightly soluble in cold alcohol, soluble in hot; essentially insoluble in water, hot or cold. Alcohol is the best solvent for it.

The appearance of iodide and nitrite, as well as bromide, among the products of the reaction shows that other organic compounds were present beside the phenetole. They were undoubtedly contained in the mother liquors and the two oily fractions, but as yet we have not had time to study these thoroughly. From the first oily portion we isolated a substance melting at 149° but in too small quantity to determine whether it was pure, or to make an analysis. We hope one of us will be able to continue this work.

When the iodtribromnitrobenzene was heated with sodic ethylate solution, tests for bromide, iodide and nitrite were

obtained after 15 minutes, but the product was an uninviting tar, from which we did not succeed in isolating any definite compound in the time at our disposal.

Sodic methylate was much less active; after it had stood with the iodtribromnitrobenzene for 10 days at ordinary temperatures, no precipitate had been formed, and although the solution gave a test for a bromide and an iodide and a very faint one for a nitrite, the organic material seemed to consist mostly of the unaltered substance; and the same results were obtained from a mixture heated on the steam bath for 15 minutes.

The 1-iod-2,4,6-tribrom-3-nitraniline is very inert toward aniline. Two grams of it were heated on the steam bath for 10 days with 10 cc. of freshly distilled aniline. At the end of this time only a faint test for bromide could be obtained, and although the organic product was brown, several crystallizations from alcohol showed that it was made up principally of the unaltered substance melting at 144°–145°.

Cambridge, Mass.
October 14, 1912

REACTIONS OF OZONE WITH CERTAIN INORGANIC SALTS

By Yoshito Yamauchi

Several workers, among whom we may mention Schönbein, Williamson, Maquenne and Mailfert, have studied the oxidation of certain inorganic salts by ozone, but report, for the most part, only the final products of the reactions and not the way in which the ozone has acted to bring them into existence. The author has therefore, at the suggestion of Prof. M. Chikashige, sought to get more accurate information upon this point, and presents the following as a brief account of his investigation:

I. Method of Investigation

Estimation of the Ozone which is to be Used for Oxidation.— To determine the concentration of ozonized oxygen before consuming it, there has existed only one method, that of di-

rectly weighing a certain known volume of it and of comparing this weight with that of an equal amount of pure oxygen. Since this method is by no means convenient, the author contrived a new one, that of filling two large cylindrical glass tubes of known volumes with one and the same sample of ozone, so that he could use one for the purpose of estimation and the other for the oxidation.

Take two tubes, *A* and *B*, of nearly equal capacity, 35 cm. in length and about 5 cm. in diameter. They are provided with glass cocks, *a* and *a′*, at one end, and with double cocks, *b* and *c* and *b′* and *c′*, at the other. They are mounted in a somewhat slanting position and connected with a bent tube at the lower end. Fig. I represents the arrangement. Keep-

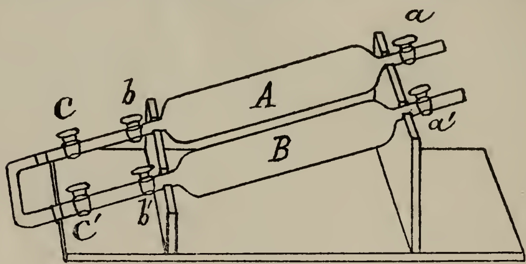


Fig. I.

ing now all the cocks open, ozonized oxygen is passed first from *A* to *B*, then from *B* to *A*, the amount of the gas passed each time being almost 1.5 times more than the total volume of the two tubes. Working regularly in this manner, it was always found that the amount of ozone in both tubes stood almost in a constant ratio, as will be seen below.

Comparison of the Amount of Ozone in the Two Tubes.—After having filled the tubes with ozonized oxygen, close all the cocks except *c* and *c′* and disconnect the tubes. Take then 2 aliquot portions of a neutral potassium iodide solution and pour them each into two different beakers, from which transfer them separately into the spaces between *b* and *c*, and *b′* and *c′*, respectively. Then, shutting off the cocks *c* and *c′* and open-

ing the others, b and b', let the solutions into the cylindrical parts of the tubes, and shake vigorously until they no longer give the odor of ozone. The solutions now containing liberated iodine are thoroughly washed down into their original vessels, and, after being acidified with a few drops of dilute sulphuric acid, are titrated for iodine by means of a standard solution of sodium thiosulphate.[1] The amounts of the ozone corresponding to these quantities are calculated from the well established equation:

$$O_3 + 2KI = K_2O + O_2 + I_2 \qquad (1)$$

The amount of ozone thus found in the two tubes is compared after being recalculated on the basis of a liter volume and the mean ratio taken from six such determinations, as will be seen from the following table:

Table I

	Ozone in gram		Ozone in gram		
No.	Per 671 cc. (Tube *A*)	Per liter (*a*)	Per 693 cc. (Tube *B*)	Per liter (*b*)	*a*/*b*
1	0.0058	0.0087	0.0062	0.0089	0.98
2	0.0053	0.0080	0.0058	0.0083	0.96
3	0.0048	0.0071	0.0044	0.0064	1.11
4	0.0081	0.0120	0.0087	0.0126	0.95
5	0.0032	0.0048	0.0032	0.0046	1.04
6	0.0147	0.0219	0.0151	0.0217	1.01
				Mean,	1.01

Now, by the aid of this, we can easily calculate the amount of ozone in one tube, upon actually finding that in the other.

Manner of Ozone Decomposition during the Process of Oxidation.—Taking a known amount of ozone, the author caused it to act upon a salt in solution, whose amount was known and was greater than one equivalent as compared with the ozone used. When the reaction was over, he estimated the amount of the oxidized salt, from which, by taking account of the amount of ozone used, he could directly infer how the ozone decomposed before the oxidation; whether as

$$O_3 = O_2 + O \qquad (2)$$

[1] Cf. Treadwell and Anneler: Z. anorg. Chem., **48**, 87 (1906).

where only one-third the oxygen atoms would have entered into the reactions, or as

$$O_3 = 3O \tag{3}$$

where all three atoms would have taken part in the oxidation. With the aid of such inferences, he established chemical equations to represent the oxidizing action of ozone according to the various cases.

II. Reactions of Ozone Investigated according to this Method

1. Arsenious Acid.—That metallic arsenic is oxidized by ozone finally to arsenic acid was first made known by Schönbein.[1] The determination of ozone by the use of arsenious acid[2] is based on this reaction.

The author took a known amount of ozone contained in a cylindrical tube, let in an aliquot portion of a neutral potassium arsenite solution, and allowed the mixture to react for about half an hour, the quantity of the oxidized salt being then calculated from the amount of the unchanged arsenite, as determined by the use of a standard iodine solution. The ratio of the ozone to the arsenite oxidized is given in the following table:

Table II

No.	Ozone in gram	Arsenious acid oxidized by the ozone in gram	Arsenious acid per gram ozone in grams
1	0.0093	0.0204	2.19
2	0.0080	0.0149	1.86
3	0.0059	0.0138	2.34
4	0.0116	0.0243	2.10
5	0.0098	0.0215	2.19
		Mean,	1 : 2.14

This reaction is, therefore, well represented by the usual equation:

$$As_2O_3 + 2O_3 = As_2O_5 + 2O_2 \tag{4}$$

as it requires 2.06 grams arsenious oxide per gram ozone.

[1] Ann. Chem. (Liebig), **89**, 288 (1854).

[2] Thénard: Compt. rend., **75**, 174; Hartley, J. Chem. Soc., **39**, 120 (1881). Treadwell and Anneler: Z. anorg. Chem., **48**, 94 (1906).

2. *Stannous Chloride.*—The conversion of a stannous into a stannic salt by ozone has been studied by Schönbein[1] and Williamson.[2] If the reaction is, as in other cases,

$$3SnCl_2 + 6HCl + 3O_3 = 3SnCl_4 + 3H_2O + 3O_2 \quad (5)$$

the amount of the stannous chloride oxidized by ozone would be in the ratio of 3.96 grams to 1 gram of the latter. But, if the reaction takes place as follows:

$$3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O \quad (6)$$

the ratio would be 11.87 grams stannous chloride to 1 gram ozone; besides, the pressure in the reaction tube would be then very much reduced, since oxygen is no longer produced in a volume equal to the ozone consumed.

According to the author's experiments, the reaction seems to proceed exactly as shown in Equation (6), and not as in (5). After a known quantity of a stannous chloride solution in hydrochloric acid had been mixed in the usual manner with a known quantity of ozone, and left for about half an hour with constant shaking, the amount of the stannous chloride entering into reaction was calculated from the amount of the unoxidized salt, which was found by the use of a standard iodine solution, subtracted from the total amount of the salt taken. The results of the experiments are given in the following table:

Table III

No.	Ozone in gram	Stannous chloride oxidized by the ozone in gram	Stannous chloride per gram ozone in grams
1	0.0077	0.1147	14.89
2	0.0119	0.1550	13.03
3	0.0089	0.1392	15 64
		Mean,	1 : 14.52

This ratio nearly coincides with that calculated from Equation (6). That it is a little more than the latter is due, perhaps, to the simultaneous action of the co-existing ordinary oxygen. It must, however, not be forgotten that what causes the re-

[1] Ann. Chem. (Liebig), **89**, 293 (1854).
[2] *Ibid.*, **61**, 14 (1847).

action for the main part is the ozone and not the oxygen, because the reaction goes on very rapidly only at first, and as soon as the ozone is used up, the reaction becomes notably slower. Thus, the two tubes, *A* and *B*, were equally filled with ozone, and treated with equal quantities of a stannous chloride solution. One of the tubes was then left for only 20 minutes, and the other for a much longer interval of time. The oxidation stopped after a certain lapse of time; the degrees of oxidation in both tubes, expressed in terms of the stannous chloride, were nearly the same in spite of so great a difference in time. The results of four such experiments are given in Table IV.

Hence, we have here a new instance of oxidation by ozone, in which the latter acts by decomposing itself according to Equation (3).

Table IV

Time in minutes	Degrees of oxidation in terms of stannous chloride	t'/t
20	0.1368	1/1.07
140	0.1468	
20	0.2015	1/1.05
100	0.2120	
20	0.1795	1/1.15
60	0.2062	
20	0.2255	1/0.95
40	0.2133	
	Mean,	1 : 1.06

3. Sodium Thiosulphate.—The action of ozone on sodium thiosulphate seems not to have been studied hitherto by any chemist. When a solution of this salt is shaken with ozone, it becomes milky through the separation of sulphur, while the solution, which remains quite neutral during the reaction, contains sulphite and sulphate, besides some unchanged thiosulphate.

Whether or not a part of the sulphite and sulphate comes from the oxidation of the precipitated sulphur by ozone cannot yet be definitely decided, because sulphur is oxidizable, according to Mailfert,[1] while according to Schönbein[2] it is not.

[1] Compt. rend., **94**, 1186 (1882).
[2] Ann. Chem. (Liebig), **89**, 282 (1854).

With regard to the author's experiment, in which he passed ozone a long time through the precipitated sulphur, with neutral reaction, suspended in water, he could find only an almost insignificant quantity of sulphite formed. However, in order to make the problem as simple as possible, he did not take into account the presence of sulphite from such a source.

Then, the quantitative estimation of the reactions was effected in the following manner:

As usual, a known amount of a sodium thiosulphate solution was introduced into the tube containing a known amount of ozone, and the mixture was allowed to stand for about half an hour with frequent shaking. After being separated from the precipitated sulphur, the solution was then examined for its iodine equivalent (6, V) (the latter covers the amount of both the thiosulphate in excess and sulphite). Barium chloride was added to this solution, precipitating all the sulphates, a part of which had been originally present through the oxidation of the thiosulphate by ozone, and the rest derived from the sulphite oxidized by iodine. The amount of the sulphates (1, V) therefore corresponded to the total weight of the thiosulphate entering into reaction (2, V) with a definite volume of ozone: cf. Equation (9). Then, from the excess (4, V) of the thiosulphate originally taken (3, V) over that actually entering into reaction (2, V), may be directly calculated its iodine equivalent (5 V), and the difference (7, V) between this value and that determined before (6, V), which is a little greater, gives exactly the amount of the sulphite, the amount of the thiosulphate corresponding to it being then calculated from it (8, V). The amount of the thiosulphate changing into the sulphate (9, V) can be also calculated by taking the difference of the above quantity from the total amount of the thiosulphate entering into the reaction (2, V). The ratio of the thiosulphate changing either into the sulphite or into the sulphate becomes nearly 1 : 2 from the mean of four such experiments, as will be seen from the following table:

Table V

No.	Description	I	II	III	IV
1	Barium sulphate (found)	0.0733	0.1244	0.0826	0.1024
2	Sodium thiosulphate entering into reaction (calc. from 1)	0.0496	0.0843	0.0560	0.0694
3	Sodium thiosulphate originally taken (found)	0.1606	0.1606	0.1606	0.1606
4	Excess of sodium thiosulphate escaping the reaction (diff. between 3 and 2)	0.1110	0.0763	0.1046	0.0912
5	Iodine equivalent to the above salt (calc.)	0.0891	0.0613	0.0840	0.0732
6	Iodine equivalent to the thiosulphate solution soon after the reaction with ozone (found)	0.1146	0.1142	0.1144	0.1148
7	Difference between 5 and 6	0.0255	0.0529	0.0304	0.0416
8	Sodium thiosulphate changing into the sulphite[1] (calc. from 7)	0.0159	0.0329	0.0190	0.0259
9	Sodium thiosulphate changing into the sulphate (diff. between 2 and 8)	0.0337	0.0514	0.0370	0.0435
10	Ratio of 8 to 9	1 : 2.1	1 : 1.6	1 : 2.0	1 : 1.7
			Mean,	1 : 2	

[1] From the equation, $2I + Na_2SO_3 + H_2O = 2HI + Na_2SO_4$, we see that two atoms of iodine are equivalent to 1 molecule of sodium sulphite, which is now in its turn equivalent to one molecule of sodium thiosulphate.

Hence we find that 2 molecules of sodium sulphate are always produced together with 1 molecule sodium sulphite. Perhaps we have no other way of understanding this reaction than by supposing it to take place in two successive stages. The first is the catalytic decomposition of the thiosulphate into sulphite and sulphur, where the ozone effects no oxidation at all; thus

$$3Na_2S_2O_3 = 3Na_2SO_3 + 3S \qquad (7)$$

Then follows the second stage, in which only two out of the three molecules of sodium sulphite are acted upon by ozone, so that the reaction may be expressed as follows:

$$2Na_2SO_3 + 2O_3 = 2Na_2SO_4 + 2O_2 \qquad (8)$$

Since we know the amount of ozone necessary to effect the oxidation of thiosulphate, as shown in (9, V), into sulphate, we can calculate the amount of the oxidized thiosulphate per gram ozone, thus:

Table VI

No.	Ozone in gram	Sodium thiosulphate changed into the sulphate in gram	Sodium thiosulphate per gram ozone in grams
1	0.0101	0.0337	3.34
2	0.0173	0.0514	2.97
3	0.0111	0.0370	3.33
4	0.0139	0.0435	3.13
		Mean,	1 : 3.19

Calculated for 1 molecule sodium thiosulphate per molecules ozone, as may be deduced from equation (8), we have the ratio 1 : 3.29, which is really in good accord with the experimental ratio.

Combining now the 2 equations (7) and (8), we establish the following to account approximately for the whole course of the reaction of ozone with sodium thiosulphate:

$$3Na_2S_2O_3 + 2O_3 = 2Na_2SO_4 + Na_2SO_3 + 2O_2 + 3S \qquad (9)$$

4. *Thallous Nitrate.*—Schönbein[1] first studied the oxidation of thallium or thallous hydroxide by ozone in the presence of water. Schöne[2] applied this reaction to the quantitative

[1] J. prakt. Chem., **93**, 36 (1864); *Ibid.*, **95**, 470 (1865).
[2] Ber. d. chem. Ges., **13**, 1508 (1880).

analysis of ozone, making use of test paper soaked in thallous hydroxide solution, where the depth of the color of the thallic oxide formed should vary according to the amount of ozone present. Lamy[1] settled the composition of thallic oxide, dried at 100°, to be $Tl_2O_3.H_2O$, while Rabe[2] claims to have obtained the anhydrous oxide, Tl_2O_3, by oxidizing an alkaline solution of a thallous salt with hydrogen peroxide.

According to the author's experiments, the water in the thallic oxide seems never to be equal to one molecule, as was shown by Lamy. So, it may be urged that hydrated thallic oxide is very liable to lose its water in part even when dried below 100°. He also determined as usual the amount of thallic oxide precipitated equivalent to the ozone used, from the results of which the equation for the reactions could be well established.

An ammoniacal solution of thallous nitrate was taken for the purpose of experiment. An aliquot portion, after being introduced into the tube containing ozone, was shaken vigorously for a few minutes only. The voluminous brown precipitate was then washed, collected on a weighed filter, dried in an air bath below 100°, and finally weighed. The results of the experiments are given in the following table:

Table VII

No.	Ozone in gram	Thallic oxide precipitated by the action of ozone in gram	Thallic oxide per gram ozone in grams
1	0.0206	0.1038	5.04
2	0.0151	0.0618	4.09
3	0.0201	0.0952	4.74
4	0.0147	0.0750	5.10
5	0.0139	0.0716	5.15
6	0.0182	0.0857	4.71
7	0.0139	0.0635	4.57
		Mean,	1 : 4.77

If the reaction be represented as follows:

$$2TlOH + 2O_3 = Tl_2O_3 + H_2O + 2O_2 \qquad (10)$$

and the oxide be considered to retain no water at all, then the

[1] Ann. chim. phys., [3] **67**, 385.

[2] Z. anorg. Chem., **48**, 428 (1906).

ratio of ozone to the oxide formed is 1 : 4.76, in good accord with the experimental data.

Now, in the hope that the composition of thallic oxide might be better established, the author converted 0.5096 gram of well dried oxide into thallic chloride, added a certain quantity of potassium iodide, and then determined the amount of iodine liberated from it. The amount of thallium equivalent to iodine was calculated from the equation,

$$TlCl_3 + 3KI = TlI + 3KCl + I_2 \qquad (11)$$

and then recalculated to thallic oxide, Tl_2O_3, with no water, as 0.4970 gram. The loss of weight from the original 0.5096 gram, about 2.4 per cent., may be due to some quantity of water still retained.

That the oxidation of a thallous salt by ozone goes on rapidly and completely, and that the thallic oxide thus formed can be very easily weighed, affords surely another very convenient method for the gravimetric determination of ozone, in contrast to that of Schöne.[1] It is then only necessary to take proper care to dry the oxide always at a constant temperature, in order to have the water regularly expelled.

5. *Mercurous Nitrate.*—According to Mailfert,[2] mercurous salts in solution are easily oxidized by ozone partly to mercuric salts, which go into solution, and partly to basic salts, which remain undissolved.

The author examined the action of ozone on mercurous nitrate in the presence of an excess of nitric acid, and found that the oxidation takes place, though very slowly and incompletely, there remaining always some odor of ozone. The formation of basic salts was not perceived, because there was present much excess of nitric acid.

The amount of the mercuric salt formed was determined from the quantity of the unchanged mercurous salt remaining, which was precipitated and weighed in the form of chloride. The results of the experiments are as follows:

[1] *Loc. cit.*

[2] Compt. rend., **94,** 860 (1882).

Table VIII

No.	Ozone in gram	Mercurous nitrate oxidized by ozone in gram	Mercurous nitrate per gram ozone in grams
1	0.0100	0.0919	9.19
2	0.0066	0.0614	9.30
3	0.0108	0.1090	10.09
4	0.0110	0.1101	10.01
5	0.0090	0.0807	9.63
		Mean,	1 : 9.64

Calculated for the equation,

$$Hg_2(NO_3)_2 + O_3 = HgO + Hg(NO_3)_2 + O_2 \quad (12)$$

the ratio of ozone to mercurous nitrate is 1 : 10.94, wherein the difference from the experimental data shows the incompleteness of the reaction.

6. *Ferrous Ammonium Sulphate.*[1]—A solution of this salt was treated in the usual manner with ozone, and the amount of oxidized salt was determined by subtracting the unchanged ferrous salt, as determined with potassium permanganate, from the total quantity of ferrous salt originally taken. The ratio of the ozone to the oxidized salt was found from the following data:

Table IX

No.	Ozone in gram	Ferrous ammonium sulphate oxidized by ozone in gram	Ferrous ammonium sulphate per gram ozone in grams
1	0.0023	0.0332	14.43
2	0.0111	0.1484	13.37
3	0.0047	0.0666	14.17
4	0.0064	0.0809	12.64
		Mean,	1 : 13.65

Calculated for the equation,

$$2Fe(NH_4)_2(SO_4)_2 + O_3 = Fe_2O(SO_4)_2 + 2(NH_4)_2SO_4 + O_2 \quad (13)$$

the ratio is 1 : 11.83. The difference between the experimental ratio and the theoretical must be due to the simultaneous action of ordinary oxygen, as we have seen in the case of stannous chloride.

[1] Schönbein, Ann. Chem. (Liebig), **89**, 293 (1854), makes the statement that the ferrous salt is oxidized by ozone to the ferric state.

7. *Tellurous Oxide.*[1]—By passing ozone into tellurous oxide suspended in water, no appreciable amount of oxidation products could be detected.

8. *Titanium Dioxide.*—Since titanium dioxide dissolved in concentrated sulphuric acid is very easily oxidized by hydrogen peroxide, the author made certain tests as to whether it is also oxidized by ozone. The results, however, were always negative.

9. *Chloropalladious Acid.*—According to L. Wöhler and King,[2] oxidation of this compound by ozone takes place in the following manner:

$$H_2PdCl_4 + 4H_2O + O_3 = Pd(OH)_4 + 4HCl + H_2O + O_2 \quad (14)$$

But, as there was found no convenient way of distinction between the palladic and palladious compounds, the author could not apply his method to test the correctness of the above equation.

SUMMARY

1. As the concentration of ozone differs with every preparation, all methods of determining the concentration through the consumption of the gas must involve using up the preparation, i. e., when the concentration is known, the preparation no longer exists. The method of its determination by direct weighing is also not convenient. The author has, therefore, contrived a new method of dividing one sample into two parts, and of determining the concentration of the one by measuring that of the other by analysis.

2. So far as the author could determine, ozone seems to be decomposed according to the equation

$$O_3 = 3O$$

only in the case of the oxidation of stannous chloride. The decomposition goes on, however, usually as follows:

$$O_3 = O_2 + O$$

3. The action of ozone on sodium thiosulphate has been studied by the author perhaps for the first time. There take

[1] Cf. Mailfert: Compt. rend., **94**, 1186 (1882).

[2] Z. anorg. Chem., **46**, 327 (1905).

place two reactions, in which the ozone seems first to cause the catalytic decomposition of the thiosulphate and then to be able to effect a partial oxidation of the sulphite formed.

4. Formation of thallic oxide from a thallous salt by ozone occurs very rapidly and completely. It may surely be utilized as a gravimetric method in the quantitative determination of ozone.

KYOTO, Sept. 20, 1912

[Contributions from the Sheffield Laboratory of Yale University]

HYDANTOINS

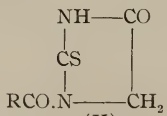
THE ACTION OF THIOCYANATES ON α-AMINO ACIDS

[TWENTIETH PAPER]

BY TREAT B. JOHNSON

The writer desires to call attention, in this note, to an error which unfortunately occurs in some of the recent publications from this laboratory on thiohydantoins. It has been shown that an acyl derivative of an α-amino acid (I) (hippuric acid, etc.) enters into an important reaction with a thiocyanate in the presence of acetic anhydride and acetic acid. They combine, forming the corresponding acylthiohydantoins (II) as represented by the equation below. Of the several α-amino acids so far examined, glutaminic and aspartic acids are the only ones which have failed to react in this manner.

$$\underset{\text{(I)}}{RCONHCH_2COOH} + KSCN(\text{or } NH_4SCN) \longrightarrow$$



(II)

During the progress of our investigation of this interesting class of sulphur compounds my coworkers generally reported excellent yields by application of this reaction, but sometimes, however, the results obtained were very unsatisfactory. At first, no explanation could be offered for these failures, but it finally developed, after many experiments by the writer, that

the results were always unsatisfactory when we used potassium thiocyanate from a certain bottle, which had been in stock for fully six years. On the other hand, the other specimens of potassium thiocyanate, which were imported from Kahlbaum specially for our investigation, gave excellent results.

I now find that all of our thiocyanate (6 kilograms), with the exception of the bottle which failed to give the results desired, is mislabeled and is pure ammonium thiocyanate instead of potassium thiocyanate as represented by the Kahlbaum label. Consequently the yields given in the following publications: *Journal of the American Chemical Society*, **33**, 1974; *Journal of Biological Chemistry*, **11**, 97; THIS JOURNAL, **47**, 242; **48**, 103, were obtained by using ammonium thiocyanate instead of the potassium salt.

The most striking difference in behavior is observed when applying our reaction to hippuric acid. The product of the reaction is the same with both salts, but with potassium thiocyanate the product is oily and solidifies only after long standing, while, on the other hand, the ammonium salt reacts smoothly under similar conditions, giving a hydantoin which solidifies immediately on pouring into water.[1] Because of the remarkable difference in behavior of these two thiocyanates towards hippuric acid, we are now making a comparative study of their action on other α-amino acids.

The writer has always had the greatest confidence in the purity of Kahlbaum's preparations, but from his experience in this case and others it is evident that it will be necessary, hereafter, to test their reagents and not trust to their label.

NEW HAVEN, CONN.
Nov. 11, 1912

OBITUARY

JOHN WILLIAM MALLET

After a brief illness, Dr. Mallet closed his useful and honored life on Nov. 6, 1912, at the University of Virginia where he

[1] Mr. Marston L. Hamlin, of the Harriman Research Laboratory, New York City, writes me that he also obtained unsatisfactory results when he attempted to prepare benzoylthiohydantoin from hippuric acid and potassium thiocyanate. It is a pleasure to record my appreciation of the spirit that has characterized his correspondence.

had served as professor for forty years. Dr. Mallet was born of English parents near Dublin, Oct. 10, 1832. His father, Robert Mallet, was a civil engineer and a Fellow of the Royal Society. While at a classical school in Dublin, he developed interest in physics and chemistry through reading in his father's library the works of Black, Lavoisier, Fourcroy, Davy, Thomson, etc.

In 1848, he began analytical chemistry under Dr. James Apjohn, lecturer on chemistry at the Royal College of Surgeons in Dublin, and received private practical instruction in his laboratory. In 1849 he entered Trinity College, University of Dublin, and in that year published in the *Journal of the Geological Society of Dublin* a paper entitled "A Chemical Examination of Killinite." During the following three years he assisted his father in experiments upon the velocity of transmission of shocks from gunpowder explosions through rock and through loose earth, and also in the preparation for the British Association of an earthquake catalogue of 597 pages, extending from 1606 B.C. to 1842 A.D., all of which matter was collected and collated through a large amount of reading in different public libraries by the son before he was twenty-one years of age.

In 1851 he studied and worked under Professor Wöhler and formed a friendship with him which was kept up through life by numerous kindly letters. In 1852 he received the degree of Ph.D. at Göttingen, his thesis being a report upon the chemical examination of Celtic antiquities in the Museum in Dublin. During two vacations, he, with his fellow student, Wm. S. Clark, of Massachusetts, traveled through many manufacturing cities and mining districts of central Europe, so obtaining much information upon chemical manufactures at first hand.

In 1853 he came to the United States, primarily to collect certain engineering information for his father. Here he joined his friend, Dr. Clark, then professor of chemistry at Amherst, Mass., and shortly Dr. Mallet was elected professor of analytical chemistry in that college, where he remained but one session. The next year he was appointed chemist to the Geological Survey of Alabama, and professor of chemistry at the University of Alabama, and here he remained until 1861.

It was during these years he published in the *American Journal of Science* the analyses of a number of rarer minerals, mostly from American localities—beryl, tin pyrites, idocrase, schrötterite, etc.,—numerous analyses made for the Geological Survey and in 1856 a re-determination of the atomic weight

of lithium, also in 1857 a report upon the atomic weight of aluminum.

In May, 1862, Dr. Mallet, then, as always, a British subject, was given general supervision of the manufacture of ammunition for the Southern Confederacy, in which capacity he was most actively engaged throughout the war. This work was pushed on with such indomitable courage, patience, wisdom and skill that at the time of the surrender there was a large supply of ammunition on hand, stored near Macon, Ga.

In 1865, following peace, Colonel Mallet soon was employed by some northern capitalists to search for petroleum in Louisiana and eastern Texas. In the fall of that year he entered upon the duties of professor of chemistry in the medical department of the University of Louisiana, at New Orleans (since, Tulane University), and then organized a practical laboratory course in chemistry for medical students. During the three years passed here he devoted much time to the study of medicine and before leaving received the degree of Doctor of Medicine. This cultivation of an interest in the chemical side of medicine resulted in after years in a number of investigations in this line.

In the spring of 1868, Dr. Mallet came to the University of Virginia to organize and build up the School of Analytical and Industrial Chemistry, and in this he conducted what is thought to be the first systematic course in industrial chemistry in the United States. As an adjunct in teaching the latter course, he accomplished the collection of an extensive and comprehensive museum of chemical manufactures probably not surpassed in this country.

Here he built up the school from which came many of the teachers of chemistry in the colleges of the southern states and numbers of industrial chemists. In 1872 he was made professor of general and industrial chemistry, which work he conducted until in 1883 he accepted a professorship in the University of Texas. The next year he received a similar appointment at the Jefferson Medical School in Philadelphia and in the following session returned to his work at the University of Virginia, and remained there until his death.

As a lecturer he was most systematic, concise and deliberate, sparing no pains to present every thought and illustration with decisive clearness. His lectures made an indelible impression upon the teachable students.

Long is the roll of those who will ever recall with thankfulness the privilege of sitting under his teaching, realizing they were obtaining some insight into the wonders of nature from a master

mind and master worker; many, too, there receiving an inspiration which in after years led to vigorous research and confident initiative in the pursuit of their profession.

Dr. Mallet published in all over 100 papers upon unfamiliar chemical compounds, peculiar minerals, chemical and physical phenomena, meteoric stones and irons, volcanic dust and a number relating to the chemistry of medicine.

In 1877 he was elected a Fellow of the Royal Society and in 1880 presented to this society a revision of the atomic weight of aluminum and in 1889 a revision of the atomic weight of gold.

As an analytical and consulting chemist, his services were often sought in the examination of water, ores and manufactured products. Upon many occasions he was called to serve as expert witness in medico-legal cases.

In 1880, he was employed by the U. S. National Board of Health to conduct an investigation of the chemical methods in use for the determination of organic matter in potable waters. This considerable undertaking required more than two years and in it he had the services of four assisting analysts, conducting the work in the laboratory of the Johns Hopkins University, in Baltimore, in the laboratory of the Surgeon General at Washington and at the University of Virginia.

In 1877 he delivered a course of (20) lectures at the Johns Hopkins University on the "Utilization of Waste Materials," and in 1878 a similar course on the "Early History of Chemical Industries."

Among many appointments of honor and trust he was, upon three occasions, on the Assay Commission of the U. S.; a Judge of Awards at the International Exposition of 1876 at Philadelphia; and a member of the American Committee for the International Congress of Applied Chemistry for 1903 at Berlin and for 1906 at Rome. He was one of the founders of the American Chemical Society and a fellow or member of many other scientific societies of national repute.

He was given the degree of LL.D. by the William and Mary College, Va., and by the University of Mississippi (1872); Princeton University (1896); Johns Hopkins University (1902); and University of Pennsylvania (1906).

Dr. Mallet never strove for place or power, but, in all positions and under all circumstances, quietly and simply did his duty to the best of his very superior ability, with absolute integrity and no thought of self, but kind consideration for others. He was a devout Christian, a member of the Protestant Episcopal Church, very reserved, but very direct in expression of his Faith, when there was any occasion for it.

After teaching for fifty years, Dr. Mallet accepted the offer of a retiring allowance from the Carnegie Fund, ceasing to teach, but he continued active in his professional work up to the Eighth International Congress of Applied Chemistry in which he took part shortly before his last sickness.

Dr. Mallet was married twice. His first wife was Mary E., daughter of Judge Ormond, of Alabama, his second, Mrs. Josephine (Pages) Burthe, of New Orleans. He had three children by his first wife: John O., who died Feb., 1884, in Texas, Robert W. Mallet, Attorney at Law, of Norfolk, and Mrs. Mary C. Elliott, of Savannah, Ga.

F. P. Dunnington

REVIEWS

Trattato di Chimica Organica Generale e Applicata all'Industria, Dott. Ettore Molinari, Professore di Chimica industriale alla Societa d'Incoraggiamento d'Arti e Mestieri e di Merceologia all'Universita Commerciale Luigi Bocconi in Milano. Seconda edizione riveduta e ampliata con 506 incisioni. Milano: Ulrico Hoepli. 1912. pp. xxiii + 1087. Price, L. 18.00.

The appearance of the first edition of this unique book has already been noted.[1] That a new edition is called for after only two years and that the book is being translated into English and German is evidence of the fact that it meets a real want. In no other work, to the reviewer's knowledge, can the reader so conveniently find information on the theory and practice of technical processes based on the properties and reactions of organic substances. In the present edition, while the material has not been increased in volume, many of the chapters have been completed, some amplified and a few new ones added. The greatest additions have been made in the chapters on coal tar, dyes, alkaloids, etc. The statistics of production, exports and imports have been extended to the end of 1910 and in some cases 1911. C. A. R.

Per-Acids and their Salts. By T. Slater Price, D.Sc., Ph.D., F.I.C. of the Municipal Technical School Birmingham. Monographs on Inorganic and Physical Chemistry. Edited by Alexander Findlay, D.Sc. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. vi + 123. Price, $1.00.

In this volume of 120 pages, the author has brought together

[1] This Journal, 44, 202.

all that is known on the subject of per-acids. The book is well written and very clearly expressed and contains references to all the investigations of any importance that have been carried out on this subject. It is a valuable reference book for anyone who wishes information on this subject.

J. E. G.

PRACTICAL CHEMISTRY FOR ENGINEERING STUDENTS. By ARTHUR J. HALE, B.Sc. (London), Lecturer and Demonstrator in Chemistry at the City and Guilds Technical College, Finnsbury. With an Introductory Note by PROFESSOR R. MELDOLA, D.Sc., LL.D., F.R.S. London, New York, Bombay and Calcutta. Longmans, Green & Co. 1912. pp. xix + 192. Price, $1.00.

The author has selected such material as he thinks will be of the greatest value to an engineering student and such as can be given in the limited time at his disposal. This includes experiments on the nonmetals and a few on metallic compounds, such as pigments, paints, etc.; a brief course in qualitative analysis and in volumetric and gravimetric quantitative analysis. The author has undertaken a difficult problem and one in which the personal equation of the student and the instructor plays an important role. This book could be used with certain students with success, while others would only acquire a limited manual dexterity but no understanding of the principles involved.

J. E. G.

DIE ELEKTROLYTISCHE ALKALICHLORIDZERLEGUNG MIT STARREN METALLKATHODEN. Von DR. JEAN BILLITER, Privatdozent an der Universität Wien. I. Teil. Mit 189 Abbildungen im Text. Monographien über angewandte Elektrochemie. XLI. Band. Halle a/S.:Verlag von Wilhelm Knapp. 1912. pp. x + 284. Price, M. 16.50.

The subject is to be treated in two volumes. The present volume is a compilation of the patents granted in Germany, Great Britain and the United States. The patents of each of the three nations are recorded in the chronological order of their issue; the German patents are subdivided into process and apparatus, diaphragm, construction of electrode, and material of electrode; English patents have a fifth division, electric connection; with the patents granted in the United States the divisions are omitted. Under the heading of process

and apparatus are given the claims and description, the present status in the arts, and a discussion of leading features. The introduction treats in a general way of the principles that govern the electrolytic decomposition of alkali chlorides; there are two indices, one contains the patent numbers in numerical order with the names of the patentees for Germany, England and the United States, the other the names of the patentees.

The book is a record of an immense amount of tedious but useful work patiently carried through. It is to serve as a foundation for Vol. II, which is to be devoted to a detailed description of industrial plants, and will be issued shortly.

H. O. Hofman

Handbuch der Presshefenfabrikation. Von Dr. Phil. Wilhelm Kiby, Gärungs-Chemiker und Techniker. Mit 255 Abbildungen im Text und auf 7 Tafeln. Neues Handbuch der chemischen Technologie (Bolley's chemische Technologie, dritte Folge), herausgegeben von Dr. C. Engler, wirkl. geh. Rat und Professor an der Technischen Hochschule in Karlsruhe. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1912. s. xiv + 669. Preis, geh, M. 24; geb., M. 25.50.

The present work fills a gap in scientific and technical literature which for many years has been felt by those desirous of acquainting themselves in detail with the technique of compressed yeast manufacture. No work treating this subject comprehensively has been published since 1888, the literature being limited to a small number of articles appearing at irregular intervals in one or other of the technical or trade papers.

For this reason we feel that the appearance of this work is very timely and is, therefore, to be looked upon with great favor.

The author, who has spent the greater part of his life serving this industry, treats the subject from the standpoint of the practical man. He has not merely compiled a large amount of material and incorporated the same in book form, but rather has made a most careful selection and has constantly drawn upon his experience, acquired through long years of practice, in commenting upon the relative merits and demerits of the various processes. In fact, it is this very attitude of the author

which renders the book so valuable to both student and practitioner, for he unreservedly gives to the reader the benefits of his years of practice.

Although concerned largely with the practical side of compressed yeast manufacture, the author has realized the importance, even to the experienced man, of an understanding of the theory of the processes involved, in order to enable him to more fully comprehend their value and apply his practical knowledge to greater advantage. For this reason the author has also treated the theory of compressed yeast manufacture at some length.

The various chapters of the book treat: A. Of the historical development of compressed yeast manufacture. B. The raw materials employed. C. The important constituents of the raw materials for manufacture, viz., malting, mashing, etc., and the analytical control of these operations. E. Fermentation: 1. Historical; 2. Causes; 3. Products, etc. F. Compressed yeast manufacture: 1. The old process; 2. The new aeration process.

At the end of the book are appended, in the form of a folder, 7 diagrams of compressed yeast plants working according to the old and the new methods. A survey of all German patents pertaining to compressed yeast manufacture granted since 1877 is incorporated in this valuable work, and this feature will be especially welcomed by all who wish to acquaint themselves with the various improvements in mechanical appliances and processes.

Twelve tables for simplifying the calculation of analytical results are embodied in the work, and a carefully prepared bibliography including standard works and periodical publications, German, French and English, renders the work suitable for purposes of reference.

We must express regret, however, that the author does not seem to possess any knowledge of American conditions and the researches carried on in this country in many of the fields which are closely related to compressed yeast manufacture. Otherwise the subject matter is all carefully and comprehensively treated and the numerous excellent illustrations materially

increase its value. The paper and the type are both good, and the book as a whole conforms to the high standard set by all Vieweg publications. R. WAHL

RESEARCHES ON CELLULOSE. III. (1905–1910.) By C. F. CROSS AND E. J. BEVAN. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. x + 173. Price, $2.50.

In this volume, which was delayed in order to include research work published in 1911, the authors have departed somewhat from the plan of the preceding volumes, I and II. Instead of recording in a general way the progress of industries employing cellulose as a basic material they have confined themselves to reviewing and commenting on about eighteen of what they consider to be the more important articles published during the period covered. The discussion of the subject, while showing a very deep knowledge of cellulose, is one which brings out theoretical and purely scientific information much more strongly than it does practical technical applications.

The book is divided into five chapters which cover the following subjects:

1. A general discussion of the relation of cellulose to biological science.

2. Normal cellulose and research throwing light on its constitution.

3. Cellulose esters.

4. Ligno-celluloses: their reactions and constants.

5. Technical developments. Of the 46 pages in this chapter, 24 are taken up by a discussion of the "Heart damage" of Jute, while other subjects briefly mentioned are constituents of raw cotton, textile bleaching processes, sizing paper with rosin compounds, cellulose acetate as wire insulation, etc.

The style in which this book is written renders its reading a difficult and laborious task, and it is only by very close application that its meaning can be obtained. It would probably be much more widely read if it were written in a simpler manner.

This volume will probably be of much greater value to the worker along purely scientific lines than it will to the chemist who is technically employed. E. SUTERMEISTER

PROBLEMS IN PHYSICAL CHEMISTRY, with Practical Applications. By EDMUND B. R. PRIDEAUX, M.A., D.Sc., Assistant Lecturer in Education, University of Liverpool. New York: D. Van Nostrand Co. 1912. pp. xii + 311. Price, $2.00.

This book was written at the suggestion of Prof. F. G. Donnan, and in order to gain some practical experience of the needs and capacities of students in familarizing themselves with the fundamental laws of chemistry and in learning to think in a quantitative and accurate manner, the author conducted a "problem class" in connection with Prof. Donnan's lectures to senior students at Liverpool University. The book ranges practically over the whole field of physical chemistry, the titles of the various chapters being as follows: Units and Standards of Measurement, Thermochemistry, Systems of One Component, Mixtures, Gas Reactions, Reactions in Solution, Electromotive Force, and Kinetics of Molecular and Radioactive Changes. Each section is preceded by a brief introduction, containing a summary of such information as is necessary for an intelligent working of the problems. The choice of the latter has been restricted to such as can be solved by the aid of general principles and elementary mathematics. The data for most of the problems are taken from actual published investigations, references to which are given, and the student is also frequently referred to the original sources for discussions of the principles involved. Dr. Prideaux seems to have fulfilled his task admirably, and the book should prove of great assistance to the student of physical chemistry in teaching him to apply to actual problems the principles which he learns in the lecture room. The book is provided with a list of a few frequently used mathematical formulas and with a four-place table of logarithms and antilogarithms.

C. A. R.

EXERCISES IN CHEMICAL CALCULATION. By H. F. COWARD, D.Sc., Chief Lecturer in Chemistry, Municipal School of Technology, Manchester Lecturer in the Victoria University of Manchester, and W. H. PERKINS, M.Sc., Assistant Lecturer in Chemistry, University of Leeds. London: Edward Arnold; New York: Longmans, Green & Co. pp. v + 152.

This book does not differ materially from the various "chem-

ical arithmetics" found on the market except that some of the problems in the chapter on organic analysis involve the determination of structure from the empirical composition of a given substance and one or two of its derivatives. Some of these will tax the ingenuity of the student; indeed, it would be interesting to determine how many students could solve them without knowing the answer. Most of the problems are taken from examination papers for the various classes at Manchester, and it is probably in the preparation for such examinations that this book will find its greatest use.

C. A. R.

Les Nouveautés Chimiques pour 1912. Nouveaux appareils de laboratoire, méthodes nouvelles de recherches appliquées à la science et à l'industrie. Par Camille Poulenc, Doctuer ès Sciences Avec 236 figures intercalées dans le texte. Paris: Librairie J.-B. Baillière et Fils. 1912. pp. viii + 338. Price, Fr. 4.

The present book is the 17th volume of this interesting annual. The same plan is followed as in preceding years. Almost any chemist looking through it is likely to discover some piece of apparatus described there which may prove very useful in his work. C. A. R.

VAN'T HOFF PLAQUETTE

The Dutch sculptor, Pier Pander, has, at the suggestion of Prof. Cohen, made a splendid medal plaquette (bronze) of van't Hoff. Those desiring one will write a postal card to Herr Prof. Dr. Ernst Cohen, Utrecht, van't Hoff-Laboratorium der Rijks-Universitiet. The plaquette, which is reproduced from a marble portrait relief by the same artist, will then be sent, collect on delivery, by the firm supplying them. If 100 are sold, the price will be 6.50 marks apiece; if 200 are sold, the price will be reduced to 5.50 marks.

AVOGADRO PRIZE

The Royal Academy of Sciences of Turin, at the meeting of June 23, 1912, decided to offer the sum remaining from the subscription for the memorial to Amedeo Avogadro as a

prize for a work in chemistry bearing on the law of Avogadro which may be published during the triennium 1912–14 and to open a special competition for this purpose.

The conditions of the competition are the following:

A prize, entitled the Amedeo Avogadro Prize, of L. 1500 ($300) (convertible, if desired, into a gold medal) is assigned to that competitor who shall have published in the triennium 1912–14 the best work in chemistry, either experimental or historical-critical, relating to the law of Avogadro.

The works presented will not be returned and must be written in one of the four following languages: Italian, French, German, English; and at least three *printed* copies must be sent before December 31, 1914.

The competition will end December 31, 1914, and the prize will be awarded during the year 1915.

None of the national resident or nonresident members of the Royal Academy of Turin may compete for the prize.

PAOLO BOSELLI
President

Vol. XLIX   February, 1913   No. 2

AMERICAN

CHEMICAL JOURNAL

ON THE NITRILE OF FUMARIC ACID AND THE PREPARATION OF METHYL MALEATE

By Edward H. Keiser and L. McMaster

In the synthesis of fumaric and maleic acids from acetylene by means of the iodides and potassium cyanide the nitriles of the acids were not isolated. Subsequently E. H. Keiser and J. J. Kessler[1] obtained the nitrile of fumaric acid by heating fumaramide with phosphorus pentoxide. The long, slender needles that formed as a sublimate undoubtedly had the composition of fumaric nitrile. They had a pleasant odor and when treated with alkalis gave off ammonia. In short, the behavior of the substance was such as one would expect from a cyanide. Difficulty was experienced, however, in trying to convert the fumaric nitrile into fumaric acid. This was no doubt due to the fact that the quantities worked with were small. We have now prepared the nitrile in larger quantities and have succeeded in converting it back into fumaramide and into fumaric acid, thus establishing, beyond all doubt, its constitution.

This conversion was found to take place readily by means of an alkaline solution of hydrogen dioxide,[2] the action taking place according to the equation:

[1] This Journal, **46**, 523.
[2] Ber. d. chem. Ges., **18**, 355.

$$\begin{array}{l} \text{CHCN} \\ \parallel \\ \text{CHCN} \end{array} + 2H_2O_2 = \begin{array}{l} \text{CHCONH}_2 \\ \parallel \\ \text{CHCONH}_2 \end{array} + O_2$$

The fumaramide thus formed was then transformed into fumaric acid by warming with dilute caustic potash.

Twenty-five hundredths gram of fumaric nitrile was treated with 25 cc. of a 3 per cent. solution of hydrogen dioxide and the liquid made faintly alkaline with a few drops of caustic soda solution. There was a rapid evolution of oxygen and after a short time a white precipitate separated. This was removed by filtration, and was found to be insoluble in cold water, in alcohol and ether, but was soluble in hot water, thus showing the properties of fumaramide. In determining the melting point, it became black at 232° and melted completely at 267°. For the sake of comparison a sample of fumaramide was prepared from diethyl fumarate by the action of ammonia and this behaved in the same way as that obtained from the nitrile. The melting point of fumaramide is given by Curtius and Koch[1] at 232° "with carbonization." Hell and Poliakow[2] give it at about 266°. With a second specimen of the fumaramide made from the nitrile we found that at 233° the substance became black and at 267° it melted sharply.

The fumaramide thus made from fumaric nitrile was then hydrolyzed by warming upon the water bath for one hour with dilute caustic potash. All odor of ammonia was then gone and the solution was allowed to cool and was then neutralized with dilute nitric acid. Silver nitrate was added and a white precipitate of silver fumarate was formed. This was filtered, washed and dissolved in dilute ammonia and reprecipitated by again neutralizing with nitric acid. The precipitate, after filtering and washing, was dried at 100°. On analysis the following result was obtained:

0.0628 gram substance gave 0.0543 gram AgCl.

see errata, p. 548

	Calculated for $\cancel{C_3H_2O_4Ag_2}$	Found
Ag	65.4	65.1

[1] J. prakt. Chem., [2] **38**, 478.
[2] Ber. d. chem. Ges., **25**, 643.

The dried salt deflagrated like gunpowder when heated, this being one of the characteristic properties of silver fumarate. It was also insoluble in boiling water, a fact which distinguishes it from silver maleate.

Another portion of fumaramide made from the fumaric nitrile by means of hydrogen dioxide was saponified by alcoholic potash. As the amide is only slightly soluble in absolute alcohol, the solution was boiled for 16 hours. It was then filtered and evaporated to remove the alcohol, water added, and the alkali neutralized with nitric acid. The silver salt was then precipitated, washed, dried and analyzed.

0.1016 gram substance gave 0.0877 gram AgCl.

	Calculated for $C_4H_2O_4Ag_2$	Found
Ag	65.4	65.0

Dimethyl Maleate.—This ester has heretofore been made by the action of methyl iodide upon silver maleate. We have succeeded in preparing it from methyl alcohol, maleic acid and sulphuric acid. Five grams of maleic acid, 50 cc. of methyl alcohol and 2 cc. of concentrated sulphuric acid were boiled for four hours under an inverted condenser. The liquid was then poured into an evaporating dish and the alcohol allowed to evaporate. The residue was stirred up with barium carbonate and allowed to stand in contact with it for several days. Ether was added to the mixture and the solid matter separated by filtration. The ether was removed from the filtrate by evaporation and the thick oily residue, consisting of dimethyl maleate, was distilled. Its boiling point was found to be 203°. A small quantity of a solid melting at 102° was found in the condenser; this was dimethyl fumarate. That the clear distillate was dimethyl maleate was proved by adding bromine water to a portion of it. On standing, a white solid crystalline compound was obtained. This was recrystallized from its solution in ether. It melted at 102° and had all of the properties of dimethyl fumarate.

We have also studied the action of ammonia upon dimethyl maleate. When a mixture of the ester and ammonia solution was allowed to stand several days, the oil gradually dissolved

but no precipitate of amide was formed as in the case of the dimethyl fumarate. On evaporating slowly, after the ammonia and water were removed, a thick yellowish oil remained, which became semisolid when it was stirred and was very difficult to detach from the platinum dish in which it was contained. A portion of it, when heated, acquired a red color. Another portion, when mixed with phosphorus pentoxide, gradually became hot and as the mass turned black a white sublimate came off which was condensed in an inverted funnel. This sublimate melted at from 135° to 138,° and may have been the nitrile of maleic acid. A third portion was warmed with caustic soda and ammonia was given off. In all probability this thick gluelike mass was the amide of maleic acid.

A GENERAL METHOD FOR THE PREPARATION OF THE AMMONIUM SALTS OF ORGANIC ACIDS

By Edward H. Keiser and L. McMaster

The usual method of preparing the ammonium salts of organic acids, namely, neutralizing the aqueous solution of the acid with ammonia and evaporating to crystallization, gives very unsatisfactory results owing to the hydrolytic action of water upon these salts. A study of the literature of ammonium salts of organic acids shows that comparatively few of them have been made and analyzed. In the case of dibasic acids usually only the acid ammonium salt has been prepared.

In attempting to prepare the amide of maleic acid we desired to start with the diammonium maleate, but found it impossible to make this salt by neutralizing a solution of maleic acid with ammonia and evaporating to crystallization. We, therefore, dissolved the acid in ether and conducted a stream of dry ammonia gas into the ethereal solution. A white, flocculent, rather gelatinous precipitate at first formed, this soon collected into lumps and, on continuing to pass in ammonia, changed into a white crystalline powder. Analysis showed it to be diammonium maleate.

This method of preparing diammonium maleate was found

to be applicable in a general way to the preparation of the ammonium salts of other organic acids. In those cases in which the acid was insoluble in ether some other solvent, such as absolute alcohol, or a mixture of ether and alcohol, was used. The method is dependent upon the fact that most organic acids are soluble in ether or alcohol or a mixture of the two, while the ammonium salts are insoluble and can be thrown down by means of a stream of dry ammonia gas. Very good yields are obtained by this method. The organic salts of other weak bases, such as the salts of aniline, the amines and other organic bases can, no doubt, be made in the same general way by doing away with aqueous solutions and using only alcoholic or ethereal solutions of both acid and base.

We have made, in this way, the ammonium salts of maleic, fumaric, mesaconic, citraconic, malonic and phthalic acids.

Ammonium Maleate.—This salt was precipitated from the ethereal solution of the acid by a stream of dry ammonia, as described above, washed on the filter with ether and dried in the air. It is a white, crystalline powder, not deliquescent in the air but readily soluble in water. Büchner[1] describes this salt as being deliquescent, but his compound was prepared in the wet way. This salt has an odor similar to that of acetamide.

Analyses gave the following results:

	Calculated for $C_2H_2(CO_2NH_4)_2$	Found I	II	III	IV
C	31.97	...	31.20	32.04	32.06
H	6.71	...	7.09	6.89	6.91
N	18.66	16.12	16.13	18.70	18.46

The first two nitrogen determinations were made by the Kjeldahl method and gave low results, the last two by the Dumas method. We also prepared this salt by precipitation with ammonia in a solution of the acid in absolute alcohol.

Ammonium Fumarate.—Fumaric acid was dissolved in absolute alcohol and dry ammonia conducted into the solution. A heavy white amorphous powder was at once formed. It was filtered, washed thoroughly with alcohol and ether and

[1] Büchner: Ann. Chem. (Liebig), **49**, 67.

dried in air, on a porous plate. This salt has no odor, as in the case of the diammonium maleate. It is not deliquescent but dissolves readily in water. It gave, on analysis, the following results:

	Calculated for $C_2H_2(CO_2NH_4)_2$	Found I	Found II
N	18.66	18.47	18.50

Ammonium Mesaconate.—The mesaconic acid, obtained from Kahlbaum, was dissolved in ether and dry ammonia conducted into the solution. A gelatinous precipitate was at first formed but this soon changed into a crystalline powder. The salt was filtered, washed on the filter with ether and then dried in the air. Like the ammonium fumarate, it had no odor. It was not deliquescent but dissolved readily in water. Determinations of nitrogen gave the following results:

	Calculated for $CH_3C_2H(CO_2NH_4)_2$	Found I	Found II
N	17.07	16.71	16.84

Ammonium Citraconate.—Citraconic acid (Kahlbaum) was dissolved in ether and ammonia passed into the solution. A thick colloidal solution was at first formed, but as the ammonia continued to pass into the solution this changed into a crystalline precipitate. This was filtered, washed with ether and dried in the air. Like the ammonium maleate it has an odor like that of acetamide. The salt is not deliquescent but soluble in water.

	Calculated for $CH_3C_2H(CO_2NH_4)_2$	Found I	Found II
N	17.07	16.82	16.87

The ammonium salts of malonic and phthalic acids were also made by the same general method. The ammonium malonate came down in ether solution as a fine white crystalline precipitate. It had no odor and was not deliquescent, although readily soluble in water. The ammonium phthalate was obtained as a white powder.

[Contribution from the Chemical Laboratories of Columbia University, No. 213]

A QUANTITATIVE STUDY OF SOME ALDEHYDE REACTIONS[1]

By B. G. Feinberg

INTRODUCTION

The great and constantly growing commercial importance of aldehydes makes definite methods of analysis of great value. It is, therefore, not surprising to note that the literature on the subject is quite extensive. Although a considerable amount of work has been carried out in comparing certain of the methods with a view to determining the most acccurate, it is worthy of note that little has been done to determine the general applicability of methods, nor has a systematic quantitative study of the behavior of certain typical aldehydes towards various reagents been undertaken.

On account of the reactivity of the carbonyl group, aldehydes are capable of taking part in many reactions. Those which, in addition to the aldehyde group, also have other characteristic groups will, in turn, take part in special reactions peculiar to those groups.

Methods may therefore be classified as general when the characteristic reactions of the aldehyde group alone are considered, and special when the properties of any of the other groups present are taken advantage of for purposes of analysis.

Among the general methods (*a*) the combination of aldehydes with bisulphite, (*b*) the reaction with neutral sulphite, and (*c*) the precipitation of aldehydes as hydrazones were selected for special study.

Purpose and Plan

This work was therefore undertaken:

1. To note how nearly quantitative the general methods mentioned above were with the following typical aldehydes: formaldehyde, benzaldehyde, salicylaldehyde, *p*-hydroxybenzaldehyde, anisic aldehyde and vanillin.

[1] A part of this paper was read before the section on Analytical Chemistry of the Eighth International Congress of Applied Chemistry, Washington and New York, Sept. 4–13, 1912.

2. Wherever possible, to establish conditions that would permit of the accurate determination of an aldehyde by a given method.

3. To study the effect upon the different methods ot determination of such factors as the increasing molecular weight and the presence of various groups in addition to the aldehyde group.

The purest material possible was procured, its purity ascertained by the application of well known tests, by redistillation at reduced pressure, recrystallization or sublimation. Also, wherever possible, the best tested or approved special methods were used as checks.

Wherever the results obtained, on applying a method to a pure aldehyde, did not approximate the theoretical, the conditions of the determinations were varied until those giving the best results were obtained, or the method proven to be inapplicable on account of the nature of the product or the incompleteness of the reaction.

This work was undertaken at the suggestion of Professor H. C. Sherman, and was carried out under his direction partly at Columbia University and partly at the College of the City of New York, through the courtesy of the Director of the Laboratory.

THE BISULPHITE METHOD

Bertagnini,[1] in 1853, established the fact that bisulphite combined with substances of aldehydic nature. In 1890[2] this was introduced by Schimmel and Company, for the determination of cinnamic aldehyde in cassia oil. It now plays an important part in the valuation of oils containing citral and cinnamic aldehyde. The method of determination consists in treating a known volume of oil with sodium bisulphite in a cassia flask, shaking well and allowing to stand for some time. The oil is then brought up to the graduated portion of the flask, and the volume of uncombined oil is read off. The aldehyde present is thus determined by difference.

In 1901, M. Ripper[3] suggested using a dilute bisulphite solu-

[1] Semmler: Die aetherischen Oele, **1**, 156.

[2] Gildemeister and Hoffmann: Die aetherischen Oele, 2nd Ed., p. 602.

[3] Monats. Chem., **21**, 1079.

tion with dilute aldehyde solutions, and determining the excess of bisulphite with a standard iodine solution. Ripper uses potassium bisulphite and claims good results with formaldehyde, acetaldehyde, benzaldehyde and vanillin.

The method, as applied here, was essentially that of Ripper with the exception that solutions of various concentrations were employed.

The purification of material and the conditions which gave the best results are described below.

Formaldehyde.—The formaldehyde used was Kahlbaum's pure product, which had previously shown 33.76 per cent. aldehyde by the Blank and Finkenbeiner peroxide method.[1]

Previous investigation in the Columbia laboratory[2] had shown the Romijin[3] iodine method to be admirably adapted to the determination of formaldehyde in relatively pure solutions. This method was, therefore, chosen as another means of determining the formaldehyde content of the sample used in the investigation. The author, however, slightly modified the Romijin conditions so as to use twice the amount originally suggested. The error in measuring a small amount of solution is thus decreased, and more consistent results were obtained.

The conditions as used are therefore as follows: Ten cc. of a solution of formaldehyde of about 0.5 per cent. strength were treated in a stoppered Erlenmeyer flask with forty cc. of a standard iodine solution, about tenth normal, made up with thirty-five grams potassium iodide per liter, ten cc. normal sodium hydroxide added, and allowed to stand fifteen minutes; ten cc. normal sulphuric acid were then added and the excess of iodine determined with about tenth normal thiosulphate. By means of a blank, the amount of iodine used up by the aldehyde present is ascertained, and from the factor—one gram iodine equivalent to 0.11858 gram formaldehyde—the aldehyde equivalent of one cc. of iodine solution can be obtained. The average of fourteen determinations by this method showed 33.86 per cent. aldehyde.

[1] Ber. d. chem. Ges., **31**, 2979.
[2] Williams: J. Am. Chem. Soc., **27**, 596.
[3] Z. anal. Chem., **36**, 18.

Solutions of sodium bisulphite were now used upon an aldehyde solution of the above mentioned concentration. A three per cent. bisulphite solution gave results which approached the closest to those obtained above with the Romijin method. The figures in Table I were obtained by treating 25 cc. aldehyde solution of about 0.5 per cent. strength with 25 cc. of 3 per cent. bisulphite solution, in a stoppered Erlenmeyer flask. After standing about fifteen minutes, during which a blank is run, the excess of bisulphite is titrated with tenth normal iodine and the per cent. of aldehyde calculated from the iodine equivalent of the formaldehyde, mentioned above.

Benzaldehyde.—For use with bisulphite a high grade of commercial benzaldehyde was first distilled at the ordinary pressure and that fraction which came over at 178°.5–179°.0, corrected, using a standardized thermometer, was collected and redistilled in vacuum. At 110 mm. the boiling point of the aldehyde was found to be 112°.5, corrected. The main portion was then fractionated in vacuum, and that part which distilled over at 112°.5–113° at 110 mm. was caught in an amber-colored bottle and tightly stoppered at once. Oxidation was therefore reduced to a minimum.

A one per cent. aldehyde solution in 100 cc. of 95 per cent. alcohol and 400 cc. water was prepared, and varying amounts of this solution were treated with different quantities of sodium bisulphite solutions, ranging in concentration from 1 to 6 per cent. and the excess determined with standard iodine. Results above 95 per cent., however, were not obtained. The aldehyde bisulphite compound is apparently hydrolyzed[1] very easily, for, in all cases, when the reaction mixture was titrated with iodine the end point could not be made to persist for more than an instant. If the titration were continued until a permanent end point was obtained, the amount of iodine used would almost be equal to that required by the bisulphite used alone. Attempts to render the reaction more nearly quantitative did not prove very successful. The addition of neutral sodium sulphite to diminish ionization of the acid formed during the titration appeared to give better re-

[1] W. Kerp: Z. Unters. Nahr. Genussm., **6**, 66; also Centralb., **1904**, II, 57.

sults, but still they were only about 95 per cent. of the theoretical.

The figures in the table were obtained by treating 25 cc. of the 1 per cent. aldehyde with 25 cc. of a 3 per cent. sodium bisulphite and allowing the mixture to stand about 25 minutes in a stoppered Erlenmeyer flask before titrating the excess of bisulfite.

Salicylaldehyde.—Salicylaldehyde was purified by fractionation under reduced pressure and only that which distilled at 139°–139°.5 at 160 mm. or 166°–166°.5 at 360 mm. was treated similarly to benzaldehyde. The results obtained were only about 82 per cent. of the theoretical, indicating that this aldehyde bisulphite compound was much less stable than the corresponding benzaldehyde compound. In order to ascertain whether the greater instability of the addition compound was due to the proximity of the acid hydroxyl group, experiments were conducted with *p*-hydroxybenzaldehyde and anisic aldehyde under conditions similar to those used for benzaldehyde.

p - *Hydroxybenzaldehyde.* — Kahlbaum's *p* - hydroxybenz - aldehyde was purified by sublimation and the fine, snow-white, needlelike crystals were found to have a melting point of 115°–116°. These were then used for the various determinations. With bisulphite the results were mainly 87–89 per cent. of the theoretical, thus showing that while the hydrolysis of the aldehyde bisulphite compound was greater in this case than for benzaldehyde,[1] it was considerably smaller than for salicylaldehyde. The presence and proximity of the hydroxyl group apparently influence the stability of the bisulphite addition compound.

Anisic Aldehyde.—On account of the relation between anisic aldehyde and vanillin on one hand, and benzaldehyde on the other, it was considered very interesting to determine how the former would behave in the various determinations.

Anisic aldehyde was therefore purified by repeated fractionation under reduced pressure and that which distilled at 195°–195°.5, corrected, at 205 mm. pressure, was used in the

[1] See Table I.

determinations. The results with bisulphite showed only about 90 per cent. of the theoretical amount present. This would indicate that, while the anisic aldehyde bisulphite compound was more easily hydrolyzed than that of benzaldehyde, it was not as readily hydrolyzed as the corresponding *p*-hydroxybenzaldehyde compound, and still less so than that of salicylaldehyde.

Vanillin.—Vanillin was specially purified by Isakovics by recrystallizing once from 50 per cent. ethyl alcohol, twice from 99 per cent. methyl alcohol, and once from absolutely anhydrous methyl alcohol. In order to remove vanillic acid, which was always formed when the vanillin was exposed to the air, he treated the material before the last crystallization with 1 per cent. sodium hydroxide solution sufficient to remove not only all the vanillic acid present, but also 5 per cent. of the vanillin, so as to be sure that all the acid had been taken out. He claimed that this treatment would give a vanillin about as pure as it could be made.

The vanillin prepared above, as well as materials prepared by Kahlbaum and by Fritzsche Bros., were used in the determinations.

When the conditions with bisulphite used heretofore were applied to the determination of vanillin the results of repeated determinations on the three preparations ranged from 93 to 96 per cent. of the theoretical. Attempts to make the reaction more nearly quantitative by increasing the concentration of the bisulphite, using potassium instead of sodium bisulphite or alcohol instead of water as a solvent for the vanillin, did not very materially change the figures. The vanillin-bisulphite addition product apparently is hydrolyzed to a smaller extent than any of the others tried, excepting formaldehyde.

The figures in the table were obtained by treating an approximately 1 per cent. aldehyde solution with 10–25 cc. of 3 per cent. sodium bisulphite solution in a stoppered Erlenmeyer flask and titrating after 15–25 minutes with a standard iodine solution until the blue color with starch persisted for an instant. The difference between the amount of iodine re-

Table I.—Bisulphite Results for the Different Aldehydes in Per Cent. of the Theoretical

	Formaldehyde[1]	Benzaldehyde	Salicylaldehyde	*p*-Hydroxybenzaldehyde	Anisic aldehyde	Vanillin
	98.70	93.45	80.48	88.40	89.90	A material
	98.70	92.79	81.58	88.86	90.40	95.19
	98.11	93.34	82.01	88.40	90.17	95.59
	98.46	92.02	82.23	89.10		95.21
	98.64	93.12	82.23	89.10		95.77
	98.02	93.55		85.66		95.21
	98.37	93.12		85.38		95.64
	98.08	94.98		85.50		95.20
	98.52	95.19		87.09		94.98
	98.96	94.77		86.77		B material
	98.70	92.89		87.09		94.50
	99.11	93.71				94.40
	99.44	93.61				94.50
	98.79	94.03				94.63
	99.44	93.82				94.31
Av.	98.67					94.18
						C material
						95.75
						95.75
						95.35
						95.72
						95.50

quired by a blank carried out under similar conditions and that required in the determination, gave the iodine equivalent to the amount of aldehyde used. The per cent. was calculated by using the factors obtained from the amount of aldehyde equivalent to 1 gram iodine, thus: 1 gram iodine is equivalent to 0.1186 gram formaldehyde, 0.4118 gram benzaldehyde, 0.4808 gram salicylaldehyde or *p*-hydroxybenzaldehyde, 0.5360 gram anisic aldehyde, 0.5990 gram vanillin.

W. Kerp[2] finds that the sodium bisulfite addition compounds of aldehydes and ketones are dissociated into their components in water. This is increased by a rise in temperature and lowered by an increase in concentration. He finds that the

[1] These figures were obtained by dividing the results by 33.86, the average result obtained with the Romijin method. This was done in order to make the results comparable with those in the other columns.

[2] Z. Unters. Nahr. Genussm., **6**, 66; also Centralb., **1904**, II, 57.

formaldehyde compound is most stable and gives the least bisulphite in solution; acetaldehyde gives five times as much bisulphite as the formaldehyde compound under the same conditions; benzaldehyde, thirty-one times as much; acetone, 155 times; and glucose, 500–1200 times as much as the formaldehyde compound. Titrating with iodine destroys the equilibrium between the undissociated addition compound, aldehyde and bisulphite, causing more bisulphite to form. A study of Table I will give an idea of the relative ease with which the addition compounds are probably dissociated.

Another cause for low results, though of less importance than that caused by the dissociation described above, would be the error in reading the burette. Thus, if that error be placed at about 0.01 cc. for a concentrated bisulphite solution, this would amount to about 0.1 cc. of iodine solution, which alone is sufficient to cause an error of three- to four-tenths of a per cent. on the amount of vanillin taken for an analysis.

Effect of Varying Conditions

Varying Excess of Reagent.—The effect of excess of reagent in different amounts as measured by the volume of iodine solution required to titrate the excess is shown in Tables II and III. In the first column the amount of bisulphite in excess required only about 5 to 15 cc. tenth normal iodine. In the second column a medium excess of bisulphite is used, requiring up to about 50 cc. tenth normal iodine. In the third the reagent is in still greater excess:

Table II.—Comparison of Results with Various Concentrations of Sodium Bisulphite on Formaldehyde

Excess equivalent to 5–15 cc. 0.1 N I Per cent.	Medium excess 25–50 cc. I Per cent.	Excess equivalent to about 50–75 cc. I Per cent.
96.69	99.11	97.66
97.16	99.44	98.14
95.89	98.52	
95.98	99.44	Av. 97.75
95.98	98.96	
95.98	98.70	
	98.37	
Av. 96.36	98.20	
	98.02	
	Av. 98.75	

Here the best results were obtained with an excess of bisulphite equivalent to 25–50 cc. iodine. A similar result was observed with benzaldehyde, as will be seen from Table III, which follows:

Table III.—Comparison of Results with Various Concentrations of Sodium Bisulphite on Benzaldehyde

Excess equivalent to 5–15 cc. 0.1 N I Per cent.	Medium excess 25–50 cc. I Per cent.	Excess equivalent to about 50–75 cc. I Per cent.
90.95	93.34	93.80
90.95	93.12	93.94
90.75	93.55	93.60
89.46	93.12	91.73
89.46	94.98	92.00
	95.19	92.84
Av. 90.31	94.77	92.20
	93.71	92.84
	93.61	92.62
	94.03	93.27
	93.82	92.41
	93.73	
	93.82	Av. 92.84
	Av. 93.90	

On vanillin the results obtained on decreasing the quantity of water by using alcohol as a solvent, or on substituting potassium bisulphite for the sodium compound, as well as on varying the concentration of bisulphite, are tabulated in Tables IV and V:

Table IV

0.10–0.15 gram vanillin in 50 cc. water Per cent.	0.1500–0.2000 gram vanillin in 5 cc. alcohol and 10 cc. water Per cent.
90.13	94.82
90.46	93.54
89.00	93.90
90.60	93.75
87.07	93.20
91.64	95.11
Av. 89.82	Av. 94.05

In Table V the effect of varying the concentration of sodium

bisulphite or employing potassium bisulphite on 25 cc. of a water solution of aldehyde containing 0.2000 to 0.2500 gram vanillin is tabulated:

Table V

Excess sodium bisulphite equivalent to 25–50 cc. I Per cent.	Excess equal to 50–75 cc. I Per cent.	Excess equal to about 100 cc. I Per cent.	Potassium bisulphite excess equal to about 25 cc. I Per cent.
95.40	96.37	88.64	94.75
95.70	95.72	88.72	94.63
95.40	95.72	88.06	94.82
95.70	95.59	87.40	94.63
93.22	95.21	89.05	94.50
93.22	95.77		94.40
95.00	95.21	Av. 88.39	
94.50			Av. 94.62
95.00	Av. 95.65		
94.40			
94.51			
94.82			
Av. 94.71			

It may be seen from Tables II, III and V that if the bisulphite is not in sufficient excess, the results are lower than when a considerable excess of reagent is present. If, on the other hand, the excess is still further increased, a point is reached where, because of the difficulty of handling bisulphite solutions of greater concentration and because of the decreasing stability of the aldehyde bisulphite compound (due to increasing acidity of the mixture), irregular and often much lower results are obtained. The amount of bisulphite in excess which gives the most favorable results may then be set as the one which requires about 50 cc. of tenth normal iodine to titrate in a volume of about 50 cc. The most convenient strength for this purpose is a solution of 2–3 per cent. sodium bisulphite and 25 cc. of such a solution can be handled without great error.

It may further be noted from Table V that potassium bisulphite is of the same efficiency as the sodium compound.

R. H. Williams,[1] working in this laboratory, compared the

[1] J. Am. Chem. Soc., **27**, 596.

Legler[1] ammonia method, the Blank and Finkenbeiner[2] peroxide oxidation method, the Romijin[3] iodine and potassium cyanide methods on formaldehyde. He found that the condensation methods give lower results than the oxidation methods, either because the oxidation goes further than the equation would indicate or more probably because the condensation is not quite complete. The results here obtained with the bisulphite method in the case of formaldehyde are in harmony with the conclusion reached by Williams.

THE NEUTRAL SULPHITE METHOD

According to some investigators, when neutral sodium sulphite in water solution acts on an aldehyde or ketone, sodium hydroxide is liberated thus:

$$R.CHO + Na_2SO_3 + H_2O = R.C(OH)NaHSO_3 + NaOH$$

The use of this reaction for the quantitative determination of aldehydes was first suggested by Tiemann.[4] Later Sadtler[5] stated that this reaction was more or less general for the quantitative determination of some saturated and unsaturated aliphatic and aromatic aldehydes, and some ketones. The method as worked out by him consists in titrating the alkali with normal acid. From the equation the amount of aldehyde present could be calculated.

A 20 per cent. sodium sulphite solution was prepared and neutralized as exactly as possible, phenolphthalein being used as indicator. When this solution was used with dilute aldehyde solutions, and tenth normal acid employed in the titration, the results obtained were quite far from the theoretical. This may, in part, be due to the difficulty of obtaining a sharp end point with sodium sulphite and tenth normal acid, 0.5 cc. acid, more or less, producing no effect on the end point. When, however, the concentrated aldehyde was used, normal or half normal acid could be used for the titration, and on ac-

[1] Ber. d. chem. Ges., **16**, 1333.
[2] *Ibid.*, **31**, 2979.
[3] Z. anal. Chem., **36**, 18.
[4] Ber. d. chem. Ges., **31**, 3317 (1898).
[5] Am. J. Pharm., **76**, 84 (1904). J. Soc. Chem. Ind., **23**, 303 (1904). J. Am. Chem. Soc., **27**, 1321 (1905).

count of the large amounts of acid used up, 0.1 or 0.2 cc. did not cause a serious error. The determination on formaldehyde was, therefore, carried out as follows:

Two to five grams of the 34 per cent. aldehyde solution were weighed into a stoppered Erlenmeyer flask and neutralized with tenth normal sodium hydroxide and 2 drops phenolphthalein; now 50 cc. of the neutral sodium sulphite solution were added for each 2 grams of aldehyde, the mixture allowed to stand about half an hour and titrated with half normal sulphuric acid to absence of a pink color. The amount of acid required by a blank containing an amount of sulphite equal to that left uncombined in the determination is subtracted from the amount required in the determination. This is the correction recommended by Russ[1] and Larsen. The results obtained by this method check very closely with those obtained by the bisulphite method, being almost identical with them. Sadtler,[2] however, in the case of citral, uses the same amount of sulphite as in the determination. He does not say whether that is also the condition in the case of formaldehyde. If, however, the blank contains the same amount of sulphite as the determination the results are about 0.75 per cent. less than those shown in Table II.

Benzaldehyde.—With benzaldehyde the conditions described in the Pharmacopoeia, 8th Revision, gave low results similar to those obtained with dilute solutions. As a result of comparative experiments in which the concentration of aldehyde, the amount of sulphite, the presence of alcohol or kerosene as diluent, and the interval before titration were the factors varied, the conditions which were found to be most satisfactory were as follows:

About a gram of benzaldehyde was weighed into a well-stoppered flask, 10 cc. alcohol added, then a little water, about 10 cc., to wash down the sides of the flask. The aldehyde was then neutralized with tenth normal alkali, 6 drops of 1 per cent. phenolphthalein being used as indicator. Then 50 cc. neutral sodium sulphite were added and titrated with half

[1] Mitt. Technol. Gewerb. Mus. Wien, [2] **16**, 85; Centralb., **1906**, II; 363.

[2] J. Soc. Chem. Ind., **23**, 303.

normal sulphuric acid until the pink color disappeared. A blank containing 35 cc. sulphite, the amount calculated to be left unabsorbed,[1] was carried out alongside of the determination, and the amount of acid required to render colorless subtracted from the total acid in the determination.

The alkali required to neutralize the aldehyde was calculated to benzoic acid and this weight of acid subtracted from the weight of the sample before calculating the per cent. of aldehyde. In this way results of about 99 per cent. of the theoretical were obtained for the benzaldehyde used.

A comparison of the results obtained under the Pharmacopoeia conditions and in the comparative experiments mentioned above will show the effect of increasing the amount of aldehyde and the superiority of the conditions selected over those of the Pharmacopoeia.

In the table below, the figures in Column A were obtained on 12 drops of the aldehyde as prescribed in the Pharmacopoeia.[2]

Table VI.—Comparison of Results with Neutral Sulphite on Benzaldehyde, under Various Conditions as Described Above

A Pharmacopoeia conditions Per cent.	B On small quantity of aldehyde Per cent.	C Pharmacopoeia conditions modified on 1 gram aldehyde Per cent.	D Under the author's conditions described above Per cent.
85.40	89.75	96.41	97.31
86.02	90.32	96.76	98.76
86.90	91.07	97.41	99.00
85.60	88.70	96.86	98.77
86.00		99.43	98.64
85.10		97.97	98.05
85.00		97.93	99.09
88.20		97.32	
90.10		97.10	
89.74			
88.17			
89.46			
86.00			

In Column B, the figures were obtained by employing the conditions described above on 12 drops of aldehyde. To

[1] Russ and Larsen: Centralb., **1906**, II, 363.

[2] Eighth revision.

confirm that the low results in Columns A and B were due to the small amount of material used, 1 gram aldehyde was substituted for the 12 drops and the determination carried out under the conditions prescribed in the Pharmacopoeia, 50 cc. sulphite solution being used instead of 10 cc. The results, which are quite conclusive, are shown in Column C. In the fourth column, D, the figures were obtained under the conditions prescribed above.

If, instead of titrating at once, the aldehyde is allowed to remain in contact with the sulphite, for a considerable period, the results obtained are low. Standing overnight gave figures between 83 and 86 per cent. instead of 98–99 per cent.

With salicylaldehyde and *p*-hydroxybenzaldehyde the acidity of the phenolic hydroxyl was neutralized with half normal sodium hydroxide and phenolphthalein before the sodium sulphite was added. During the neutralization or after the addition of the sulphite, colored compounds were formed which rendered it impossible to titrate with any degree of accuracy.

Anisic aldehyde behaves like benzaldehyde in that a clear solution is obtained which is not colored as with salicylaldehyde and *p*-hydroxybenzaldehyde. The determination of the end point is, however, more difficult; phenolphthalein must be added in the course of the titration, for the color is rather flitting.

The results that were obtained indicated only about 94 per cent. aldehyde when the determination was conducted under the conditions established under benzaldehyde.

In the case of vanillin, as with salicylaldehyde and *p*-hydroxybenzaldehyde, it was found very difficult to determine the end of the titration with any degree of accuracy whether the solution was titrated cold or hot. While the solution was only slightly colored when neutralized with sodium hydroxide on the addition of the sulphite, the brownish pink that developed could not be dissipated in the titration.

Attention may be directed here to the view of Seyewetz and Gibello.[1] They claim that when neutral sodium sulphite is

[1] Bull. soc. chim., [3] **31**, 691 (1904).

Table VII.—Results with Neutral Sulphite in Per Cent.

Formaldehyde[1] Per cent.	Benzaldehyde Per cent.	Salicylaldehyde Per cent.	p-Hydroxybenzaldehyde Per cent.	Anisic aldehyde Per cent.	Vanillin Per cent.
98.05	97.31	Not possible to determine with any degree of accuracy 52–54%	91.60	92.67	Not possible to determine with any degree of accuracy
98.64	98.76		89.60	94.09	
98.82	99.00		83.72	94.25	
98.11	98.77		83.18	93.46	
98.31	98.64		83.76	93.64	
98.00	98.05		76.09	92.33	
97.97	99.09		80.45	94.90	
98.70					
98.96	Av. 98.52				
Av. 98.40					

added to formaldehyde, no reaction takes place until acid is added. The bisulphite then formed combines with the aldehyde. Since the formaldehyde bisulphite compound reacts neutral to phenolphthalein the sulphuric acid does not decolorize the indicator until all the formaldehyde has entered into combination with the bisulphite.

$$2Na_2SO_3 + 2CH_2O + H_2SO_4 = 2NaHSO_3.CH_2O + Na_2SO_4$$

The writer is inclined to agree with this explanation for the following reasons:

1. When sulphite is added to the aldehyde used, the characteristic odor of the latter is not dissipated even on long standing until acid has been added in sufficient amount to form bisulphite to combine with all the aldehyde present.

2. If during the titration the acid should be poured in quite rapidly with shaking, the solution will turn entirely colorless long before it should do so. On shaking for some time, however, it turns pink again and the titration can be continued. This is observed only slightly with formaldehyde, but is very marked with benzaldehyde and anisic aldehyde. The behavior described would seem to indicate that more bisulphite was formed than could be absorbed at once; on thorough agitation, however, the reaction proceeded to completion and all

[1] The results obtained by this method were 33.32 per cent. on the average and were divided by 33.86 per cent., which was the figure obtained as the average by the Romijin method. This was done in order to make the results comparable with the other columns.

the bisulphite present was eventually used up; the titration could then be continued.

3. In the course of the titration, the pink color does not seem to diminish much in intensity until very near the end.

In the case of benzaldehyde and anisic aldehyde it was, moreover, possible to get experimental proof of the absence of a reaction liberating alkali as follows:

Five cc. of the aldehyde were pipetted into a cassia flask filled to the divisions on the neck with neutral sodium sulphite. The benzaldehyde remaining on top, the amount added, could be readily measured so that the pipette reading was verified. After standing in this way for twelve days with frequent shaking it was observed that the aldehyde on top had not changed in amount. When 5 cc. of the clear sulphite solution were pipetted out from the bottom of the flask, 1.1 cc. half normal acid were required for neutralization, while a blank of 5 cc. sulphite required 1.15 cc. of the acid. No alkali was therefore liberated. The result was similar in the case of anisic aldehyde.

In the case of the sulphite method, a considerable amount of practice is required before the results will be uniform and concordant. Gildemeister and Hoffmann[1] say that it is impossible to titrate sulphite solutions sharply, so that the end point of the reaction can only be approximately determined. In spite of this disadvantage, for concentrated solutions the simplicity of the process and rapidity of execution make this method quite popular. As may be seen from Table IV, this method gives with formaldehyde results which are fairly uniform and slightly lower than those obtained by the iodine method. Benzaldehyde also may be determined with a fair degree of accuracy. With the other aldehydes studied this method gave results much below the truth.

THE CONVERSION OF ALDEHYDES INTO HYDRAZONES

A. Use of p-*Bromophenylhydrazine.*—J. Hanus[2] suggested the use of *p*-bromophenylhydrazine for precipitating vanillin quantitatively. An attempt was therefore made to apply this method to the other aldehydes.

[1] Die aetherischen Oele, 2nd Ed., p. 604.
[2] Z. Unters. Nahr. Genussm., **3**, 531 (1900).

The solutions used were approximately of 1 per cent. concentration; wherever possible water alone was used as the solvent or only as small a quantity of alcohol or acetic acid as would be required to keep the aldehyde in solution, when the desired concentration was obtained by diluting with water.

The precipitant was prepared fresh when required by dissolving in the necessary volume of hot water and filtering before use.

Attempts to precipitate formaldehyde with *p*-bromophenylhydrazine did not result successfully; the precipitate did not settle and ran through the filter.

With benzaldehyde under various conditions the results did not show more than about 93 per cent. of the aldehyde present. The hydrazone did not form well, was sticky and gave a rather turbid filtrate. Similarly the hydrazone obtained with salicylaldehyde resembled the benzaldehyde hydrazone and indicated only about 93 per cent. of the aldehyde.

A well-formed and easily handled hydrazone, however, was formed with *p*-hydroxybenzaldehyde; 25 cc. of a 1 per cent. solution of the crystals in water containing 40 cc. alcohol to the half liter were treated with 75 cc. hot water containing in solution 2–3 times as much hydrazine as will combine with the aldehyde to be precipitated.

The precipitation was conducted at 50° C. and the precipitate allowed to stand five hours. It was then filtered on a Gooch crucible, washed with hot water to absence of a reaction with silver nitrate and dried at 105°. The weight of the hydrazone multiplied by 0.4193 gives the weight of aldehyde present.

$$HOC_6H_4CHO + C_6H_4BrNHNH_2 = HOC_6H_4CH : NNHC_6H_4Br + H_2O$$

Theoretical results were obtained under the conditions described.

Anisic aldehyde gave results in the neighborhood of 99 per cent. when 1 per cent. of aldehyde in acetic acid (90 cc. glacial acid to half a liter) was used. The precipitation was

carried out under conditions similar to those described above with the exception that the precipitate was allowed to stand one hour instead of five and was dried at 100°. The weight of hydrazone multiplied by 0.4460 gives the aldehyde present.

The conditions for the precipitation of vanillin with *p*-bromophenylhydrazine are essentially as described by Hanus;[1] 0.5 gram of the hydrazine, being 2–3 times the theoretical amount, was dissolved in 75 cc. hot water, filtered, and added to 25 cc. of the 0.75–1.0 per cent. water solution of vanillin which was previously warmed. The temperature during the precipitation was kept at about 50° C. The precipitate settles in about half an hour and is allowed to stand for about five hours; it is then filtered on a Gooch crucible, washed with hot water until the washings no longer reduce silver nitrate, dried at 100°, and weighed.

The weight of the hydrazone multiplied by 0.4739 gives the weight of vanillin present.

Table VIII.—Percentage Results with p-*Bromophenylhydrazine*

Formaldehyde Per cent.	Benzaldehyde Per cent.	Salicylaldehyde Per cent.	*p*-Hydroxybenzaldehyde Per cent.	Anisic aldehyde[2] Per cent.	Vanillin Per cent.
A well	93.55	93.24	99.82	99.50	A—
defined	91.12	93.21	100.09	99.11	98.75
precipitate	91.92	93.04	99.88	99.09	98.50
did not	93.42	93.25			99.07
form	93.05	93.44			99.18
		94.35			B—
		94.25			98.88
					98.72
					99.21
					99.40
					99.37
					C—
					99.09
					99.32
					99.25
					99.02
					98.86
					98.81

[1] Z. Unters. Nahr. Genussm., **3,** 532 (1900).

[2] The results here were corrected for anisic acid by titrating 25 cc. with tenth normal alkali and substracting the weight of acid thus found from the weight of aldehyde present before calculating the per cent.

From the table it may be noticed that those aldehydes which were solid, vanillin and *p*-hydroxybenzaldehyde, tended to give hydrazones which were most suited for quantitative determination. The lower the molecular weights of those that are liquid, the further from being quantitative are the results.

B. The Use of p-*Nitrophenylhydrazine.*—W. Alberda, van Ekenstein and J. J. Blanksma[1] found that *p*-nitrophenylhydrazine precipitated acetone, acetaldehyde and benzaldehyde quantitatively. Although they give only single determinations in each case to support their contention, the method was considered promising and was taken up more fully with the aldehydes considered in order to ascertain how generally applicable it might be.

The solutions of the aldehydes employed here were the same as those used with *p*-bromophenylhydrazine. The precipitant was dissolved in 30 per cent. acetic acid or in dilute hydrochloric acid and the solution filtered. This was prepared fresh when wanted.

When this reagent was employed with formaldehyde, a well defined precipitate formed at once and was easily handled; the results, however, were much below those obtained by the other methods, showing only about 76 per cent. aldehyde.

As a result of various trials the conditions which gave the most consistent results with benzaldehyde were as follows:

A 1 per cent. solution of benzaldehyde in 12 per cent. acetic acid was prepared; 25 cc. of this solution were diluted with 50 cc. water and 30 cc. of 30 per cent. acetic acid containing about twice as much of the *p*-nitrophenylhydrazine as demanded by theory were added. The precipitate was allowed to stand five hours, then filtered on a Gooch crucible, washed with 10 per cent. acetic acid to absence of a strong color with dilute alkali, dried in an oven at 105°–110°, and the weight multiplied by 0.4400 to obtain the weight of benzaldehyde. If the weight of benzoic acid is separately determined, by titration with alkali, and subtracted from the weight of aldehyde taken for analysis, the method proves to be about 99 per cent.

[1] Rec. trav. chim., **24**, 33 (1905).

accurate. It is, therefore, the most accurate method for benzaldehyde at present known.

For salicylic aldehyde, the conditions which gave the most nearly quantitative results were essentially the same as for benzaldehyde:

To 20 cc. of a 1 per cent. solution of the aldehyde in 15 per cent. acetic acid were added 50 cc. of water and 25 cc. of 30 per cent. acetic acid containing 0.6 gram of the hydrazine. The precipitate was allowed to stand one hour, filtered on a Gooch crucible, washed with 10 per cent. acetic acid to absence of a strong color with dilute alkali, and dried at 105°–110°. The weight of the hydrazone multiplied by 0.4747 gives the weight of aldehyde present. The figures obtained under these conditions are quite concordant, though only about 95.5 per cent. of the theoretical.

When the conditions described above were applied to the determination of anisic aldehyde, *p*-hydroxybenzaldehyde and vanillin, the results obtained were about 100 per cent., 101.5 per cent. and 102 per cent. for the respective aldehydes. After considerable variation of conditions had been tried, the *p*-nitrophenylhydrazine was dissolved in very dilute hydrochloric acid of about normal strength and added drop by drop from a pipette to the aldehyde solution which had previously been diluted with 75 cc. water. The mixture was stirred vigorously while the precipitant was added, and the precipitate allowed to stand half an hour before filtration. It was washed on the Gooch crucible with a little of the dilute hydrochloric acid and finally with water until the washings gave only an opalescence with silver nitrate. Under these conditions both vanillin and *p*-hydroxybenzaldehyde gave theoretical results. The precipitant is most stable when kept cold, and coprecipitation is minimized by adding the reagent drop by drop. Anisic aldehyde, however, under the same conditions, gave results considerably below the theoretical. The greater solubility of this hydrazone (as well as its much lower melting point, which causes a loss through volatilization on drying) are probably responsible for the lower results. When the precipitation was repeated under the conditions established above in acetic

acid solution, the figures coincided with those previously obtained, coprecipitation and decomposition of the reagent counterbalancing the errors when hydrochloric acid was the solvent.

The factors for calculating the aldehyde from the weight of the respective hydrazones are 0.4747 for *p*-hydroxybenzaldehyde, 0.5019 for anisic aldehyde and 0.5353 for vanillin.

Table IX.—Percentage Results with p-*Nitrophenylhydrazine*

Formaldehyde	Benzaldehyde[2]	Salicylaldehyde	Anisic aldehyde[1]	*p*-Hydroxybenzaldehyde	Vanillin
75.81	98.63	95.16	96.35	100.00	100.00
	98.62	95.38	96.70	99.80	99.77
	98.71	95.36	96.35	99.46	100.19
	98.12	95.42	96.60	99.63	99.99
	99.42	min.	96.80		99.92
		figs.	96.32		99.92
		94.50			99.54
		94.63	96.54		99.94
			97.21		
			97.52		
			97.00		
			96.32		
			96.75		
			96.60		

The conditions recommended above for vanillin and *p*-hydroxybenzaldehyde were decided upon after experiments were carried out in which the amount of reagent, the temperature of precipitation, and the amount and variety of acid were varied.

Blank tests on the reagent proved that it remained clear for a longer period when kept cold, at room temperature, than when kept warm, at any higher temperature. When determinations were carried out in which the solutions were kept at room temperature throughout the work, theoretical results were obtained, and no signs of incomplete precipitation were noticed.

[1] See Table VIII for comparison of results on anisic aldehyde.

[2] The figures are corrected for the acid present as described above for benzaldehyde.

Table X.—Comparison of Results Obtained with Vanillin under a Few Different Conditions

Reagent dissolved in acetic acid.[1] Best conditions Per cent.	Reagent dissolved in hydrochloric acid		
	Reagent added in bulk Per cent.	Reagent added drop by drop	
		Solution kept warm Per cent.	Solution kept cold Per cent.
102.53	101.58	101.66	100.00
102.68	101.35	101.21	99.77
102.48	101.12	100.94	100.19
102.68	101.91	100.54	99.99
102.18	101.85	100.88	99.92
102.14	101.62	100.31	99.92
102.18	101.70		99.54
102.20	101.50		
	101.82		

Table XI.—Comparison of Some Results Obtained with Anisic Aldehyde and p-*Hydroxybenzaldehyde when the Reagent was Dissolved in Acetic Acid or Hydrochloric Acid and the Mode of Precipitation Varied*

Aldehyde	Acetic acid solution under the best conditions Per cent.	Reagent dissolved in hydrochloric acid and added drop by drop	
		Solution kept warm Per cent.	Solution kept cold Per cent.
Anisic aldehyde[2]	100.90	98.83	96.32
			96.54
	100.43	99.13	97.21
			97.52
	100.34	98.79	97.00
			96.32
	100.76	98.67	96.75
			96.60
	100.65	97.83	96.35
			96.70
	100.40		96.35
			96.60
			96.80
p-Hydroxybenzaldehyde	101.82	101.12	100.00
	101.68	100.95	99.80
	101.09		99.46
	101.51		99.63

[1] The conditions in which the amount of acid and the temperature and the amount of reagent used were essentially as described under benzaldehyde and had given results closer to the theoretical than had previously been obtained.

[2] Corrected for acid present as described above.

Table XII

Aldehyde	Iodine[1] Per cent.	Bisulphite Per cent	Neutral sulphite Per cent.	*p*-Bromo-phenylhydr. Per cent.	*p*-Nitro-phenylhydr. Per cent.	Alkalimetric[2] Per cent.
Formaldehyde	100.00	98.67	98.40	.....	75.81	.....
Benzaldehyde	.....	93.90	98.52	92.61	98.70	.....
Salicylaldehyde	.....	81.70	Not possible to determine with any degree of accuracy	93.54	95.33	.....
p-Hydroxybenzaldehyde	.....	87.39	87.48	99.93	99.72	.....
Anisic aldehyde	.....	90.16	93.62	99.23	100.58 (with acetic acid) 96.73	.....
Vanillin	.....	95.5	Not possible to determine with any degree of accuracy	99.03	99.90	99.06

[1] The average result obtained with the iodine method, 33.86 per cent., was called 100.00 per cent. and the results with the other methods calculated from that basis.

[2] The Wellman method for determining vanillin by titrating with alcoholic potash (Pharm. Ztg., **1898,** 634):

One gram of vanillin is introduced into a 200 cc. stoppered flask and 25 cc. alcohol and 25 cc. half normal alcoholic potash added; the excess of alkali is titrated with half normal acid and phenolphthalein. The strength of the alcoholic potash with the addition of alcohol is first determined, and the difference between the two titrations multiplied by 0.076 gives the weight of vanillin.

$$CH_3OC_6H_3(OH)CHO + KOH = CH_3OC_6H_3(OK)CHO + H_2O.$$

A table giving the average results of the aldehydes employed with the various methods is attached for purposes of comparison.

CONCLUSIONS

The aldehyde bisulphite compounds are resolved into their components by dilute acids or alkalies. This instability of the bisulphite compound is heightened by the presence of the hydroxy group in close proximity to the aldehyde group.

By means of the bisulphite method, formaldehyde may be quite accurately determined, the amount of vanillin and benzaldehyde approximately ascertained, while in the case of salicylaldehyde, *p*-hydroxybenzaldehyde and anisic aldehyde, the results show the method to be practically worthless.

In the cases tested, the aldehydes did not combine with the neutral sodium sulphite and liberate alkali as is generally believed, but a reaction is obtained when acid is added, indicating that bisulphite is then formed and combines with the aldehyde. Under the conditions given, formaldehyde and benzaldehyde may be determined with a fair degree of accuracy by means of sodium sulphite. The method, however, gave only approximate results with anisic aldehyde, and proved inapplicable to salicylaldehyde, *p*-hydroxybenzaldehyde and vanillin.

The sulphite method as here developed is shown to give more accurate determinations of benzaldehyde than does the method of the U. S. Pharmacopoeia.

p-Bromophenylhydrazine, on the other hand, was found to give quantitative results with anisic aldehyde, *p*-hydroxybenzaldehyde and vanillin, and not with formaldehyde, benzaldehyde and salicylaldehyde.

p-Nitrophenylhydrazine proved to be quite a general precipitant for aldehydes, yielding a well formed precipitate even with formaldehyde. This reagent is very suitable for determining vanillin and *p*-hydroxybenzaldehyde. With benzaldehyde, salicylaldehyde and anisic aldehyde, the results obtained are subject to errors of 2 to 4 per cent.

The precipitation methods were found to be more accurate than the volumetric determinations for vanillin, *p*-hydroxy-

benzaldehyde, salicylaldehyde and anisic aldehyde, while the volumetric methods gave better results with formaldehyde.

In the case of benzaldehyde both the volumetric sulphite method and precipitation with *p*-nitrophenylhydrazine gave results approximating the theoretical.

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NEW YORK CITY

ON THE REACTION OF ETHYL IODIDE WITH SODIUM 1-PHENYL-3-THIOURAZOLE

BY SIDNEY NIRDLINGER, F. M. ROGERS AND S. F. ACREE

[THIRTEENTH COMMUNICATION[1] ON CATALYSIS]

(We have been aided in these researches by the Carnegie Institution of Washington.)

In 1905–06 Brunel[2] and Acree began a quantitative study of the mechanism of the reactions of alkyl halides with urazoles by measuring the conductivities of a number of urazole salts and the velocities of their reactions with various alkyl halides. It was desired then to learn whether the alkyl halides react with the urazole anions or with the anions and cations together, or with the nonionized urazole salts. This information was desired not only for the sake of studying the relation

[1] This work was completed in May, 1908.
[2] THIS JOURNAL, **43**, 505, and especially **48**, 352.

of these reactions to catalysis and reaction mechanisms in general, but also in order to investigate, if possible, any relation that might be found between the mechanism of the reactions involved and the occurrence of the isomeric O-ether and N-ether which are always formed when the salts of the oxyurazoles are alkylated.

Our theory has contained from the beginning, as an essential element, *the idea that both the ionized[1] salts and the nonionized salts must be considered in all reactions of salts*, and this theory and our equations have recently been used successfully by us,[2] and also by Stieglitz,[3] to reinterpret his very fine experimental work on the Beckmann rearrangement and the hydrolysis of imido ester salts.

One of the substances investigated by Brunel was 1-phenyl-3-thiourazole, the study of which was continued by Shadinger[4] in 1905–07. We have used this as a starting point in the present investigation and have undertaken to measure the conductivity of the sodium salt and the velocity of its reaction with ethyl iodide in absolute ethyl alcohol. The conductivity measurements have been used as a basis for determining the per cent. of ionization of the salt, although we recognize that these results are probably somewhat in error on account of the change in the ionic velocities in the concentrated solutions resulting from complex ions, the variations in viscosity and especially from the changes in solvation of the hydrated salt used (see page 122), which Goldschmidt[5] and Lapworth[6] have shown in a number of fine papers, by several independent methods, to take place in alcoholic solutions. Although these changes in fluidity and solvation act in opposing directions in their effect on the ionic mobilities, these factors probably influence both

[1] For full references to the work of Bredig, Lapworth, Goldschmidt, Euler, Acree, and Stieglitz see Acree and Johnson: This Journal, **38**, 258; **48**, 352.

[2] This Journal, **48**, 368.

[3] J. Am. Chem. Soc., **34**, 1689, 1690.

[4] This Journal, **39**, 226.

[5] Ber. d. chem. Ges., **28**, 3218; **29**, 2208; **39**, 711. Z. physik. Chem., **60**, 728; **70**, 627; **81**, 30. Z. Elek. Chem., **15**, 4, 305, 740; **17**, 684.

[6] J. Chem. Soc., **93**, 2203; **97**, 21; **99**, 1417, 2224; **101**, 2249. See also the important researches of H. C. Jones and coworkers on aqueous solutions.

the conductivities and the reaction velocities, and are being investigated.

The velocity of the reaction was determined by measuring at any time, t, the concentration $(A - x)$ of the urazole salt by titrating it with a standard solution of iodine. The iodine reacts quantitatively with the sodium thiourazole according to the equation:

$$2C_6H_5N_3C_2OHSNa + I_2 \longrightarrow 2NaI + (C_6H_5N_3C_2OHS)_2$$

the end point being very sharp in the presence of starch.[1] The concentration of the alkyl halide was represented by $(B - x)$.

The data thus secured were substituted in a general equation, discussed in other articles,[2] having such a form that we can tell at once whether the urazole anions, or anions and cations together, or the nonionized urazole salts are reacting with the alkyl halide. The equation has the form (*a*) or (*b*):

$$(a)\ \frac{dx}{dt} = K_i\alpha(A-x)(B-x) + K_m(l-\alpha)(A-x)(B-x)$$
$$= [K_i\alpha + K_m(1-\alpha)](A-x)(B-x)$$

or

$$(b)\ \frac{dx}{dt} = K_i\alpha(A-x)(B-x) + K_m\frac{\alpha^2}{V}(A-x)(B-x)$$
$$= \left[K_i\alpha + K_m\frac{\alpha^2}{V}\right](A-x)(B-x)$$

Therefore,

$$(a)\ VK_V = K_n = K_i\alpha + K_m(1-\alpha)$$

or

$$(b)\ VK_V = K_n = K_i\alpha + K_m\frac{\alpha^2}{V}$$

for *normal solutions* when $1/V$ is the concentration of the sodium phenylthiourazole. Equation (*b*) also represents the reaction as one of the anions alone, accelerated by the cations. As has been discussed before, when the data are substituted in the integral of (*a*) very good constants are obtained for both K_i and K_m, the average value of K_i being 0.435 and that for K_m being 0.17. The use of the integral of (*b*) leads to no con-

[1] Shadinger and Acree: This Journal, **39**, 259, 260.

[2] See This Journal, **38**, 258; **43**, 518; **48**, 353.

stants and we can therefore conclude that the velocity of the reaction of the sodium salt of 1-phenyl-3-thiourazole with ethyl iodide is a function of the concentration of the anions of the urazole as well as of the concentration of the nonionized sodium urazole salt:

$$(1)\ C_6H_5N_3C_2OHSNa + IC_2H_5 \longrightarrow C_6H_5N_3C_2OHSC_2H_5 + \overset{+}{Na} + \overline{I}$$

$$(2)\ C_6H_5N_3C_2OH\overline{S} + IC_2H_5 \longrightarrow C_6H_5N_3C_2OHSC_2H_5 + \overline{I}$$

The ratio $K_i : K_m$ is approximately 2.5, and we can therefore say that the anions are 2.5 times as effective in the reaction as the nonionized sodium salt. This is entirely in harmony with the reactions of ethyl iodide with sodium phenolate and sodium ethylate at 25°, the ratio $K_i : K_m = 5.65$ holding for the former and $K_i : K_m = 2.8$ having been found for sodium ethylate.[1]

The K_i and K_m used here may be the sum or product of other constants and hence may include "abnormal salt effects" of ions or molecules, a factor for viscosity, etc. Although the "abnormal salt effect"[2] seems fortunately to be small in this case, its value will be determined accurately by studying the reaction in very dilute solutions in which such physical factors as viscosity, "abnormal salt effect," etc., seem to play a very small role. This question, however, is being investigated thoroughly.

Dr. J. Chandler has continued the study of this reaction by using the anhydrous sodium urazole salt in absolute ethyl alcohol under somewhat different experimental conditions, and has found the values $K_i = 0.465$ and $K_m = 0.16$. Our slightly lower values for the reaction velocities are due to *our larger experimental errors* and to the use of the *hydrated* urazole salt, and therefore to the presence of small quantities of water, which lowers the reaction velocity. Dr. Chandler has found that the addition of sodium iodide suppresses the ionization

[1] Shrader, Robertson and Marshall: This Journal, 48, 352, 378.

[2] The "normal salt effect" is the change in the velocity of transformation of the active salt resulting from the variation in ionization accompanying changes in its concentration or the addition of another salt. We call any *additional* change in reaction velocity an "abnormal salt effect."

and reaction velocity of the sodium phenylthiourazole practically exactly the amount calculated from our theory; the "salt effect" is "normal" even when three equivalents of sodium iodide are added to one of the sodium phenylthiourazole (N/64).

Salt Catalysis

It is thus seen that the above reaction is *chiefly*, though not purely, ionic, and hence that the reaction velocity is not strictly proportional to the concentration of the ions. We have explained this deviation as due *chiefly* to the activity of the *nonionized salts*, augmented by a small "abnormal salt catalysis" resulting from changes in the physical properties of the solution, and perhaps to double compounds. In another case, that of the rearrangement of the acylhalogenaminobenzene derivatives,[1] the reaction seems to involve practically *only* the *nonionized salt*. We thus see that there are other cases in which the reactions are *chiefly*, but not necessarily entirely, *nonionic* in character, the *deviation* being due *chiefly* to the activity of the *ionized* salt, augmented perhaps by an "abnormal salt catalysis." We have already found the relative importance of the ionic and the nonionic reactions to vary very greatly with different cases. In his fine work on imido esters Stieglitz[2] noted a similar deviation from the purely ionic reaction, and used as an explanation the Arrhenius-Euler theory that the imido ester salts exert an "auto salt effect" on the reaction because they change the per cent. of ionization of the water, which was assumed to react through its ions alone.

$$(3)\quad C_6H_5C(:\overset{+}{N}H_2)OCH_3 + \overset{+}{H} + \overset{-}{O}H \longrightarrow C_6H_5COOCH_3 + \overset{+}{N}H_4$$

Our work[3] and his[4] data, and those of Van Dam[5] on the Beckmann rearrangement, have shown that Stieglitz's explana-

[1] This Journal, **37**, 410; **38**, 265; **41**, 464; **48**, 364.
[2] *Ibid.*, **39**, 29, 166, 402, 437, 586, 719. J. Am. Chem. Soc., **32**, 221; **34**, 1687.
[3] See especially This Journal, **38**, 258; **39**, 513; **48**, 352.
[4] J. Am. Chem. Soc., **34**, 1689, 1690.
[5] Rec. trav. chim., **18**, 408; **19**, 318.

tion is not wholly satisfactory. He now finds[1] that he can reinterpret both the imido ester work and the Beckmann rearrangement as *reactions of both ions and nonionized salts*, augmented by a salt catalysis proportional to the concentration of the total salt present. He has shown that our equations accord excellently with his data. Our results, however, on the reactions of alkyl halides with phenolates, ethylates, etc., show that all previous interpretations of *salt catalysis* advanced by others must be modified. Especially would we emphasize the fact that *our* "abnormal salt effect" is in certain cases a function not only of the concentrations of the inactive salts present but also of the concentrations of the reacting substances, as expressed in the equation:

$$\frac{dx}{dt} = [1 + (f)C_{salt}][K_i\alpha + K_m(1 - \alpha)](C_{salt} - x)(C_{alkyl\ halide} - x)$$

We would also call attention to the fact that the assumption that the water reacts through its ions *alone*, which were assumed to be increased in concentration by the addition of salts, is not advocated by Lapworth[2] or the writers,[3] and is not in harmony with three well known classes of facts, which have been discussed more fully by us elsewhere.[4]

(1) The same salt in the same concentration must be assumed by these colleagues to increase K_w in some cases and decrease it in others.

(2) The work of Lorenz[5] and Böhi on the hydrogen electrode and that of Kohlrausch show the ionization of water to be practically constant, whether salts, acids or bases are present or not.

(3) The value of K_w increases rapidly with a rise in temperature and the increase in the velocity of the reaction (3) with rise in temperature should involve the factor resulting from the increase in the active mass of the water as well as the factor due to the normal acceleration of the reaction through rise in temperature, which is independent of the changes in con-

[1] J. Am. Chem. Soc., **34**, 1689, 1690, 1694.
[2] Chem. News, **97**, 310. J. Chem. Soc., **93**, 2196.
[3] This Journal, **41**, 475; **48**, 369.
[4] *Ibid.*, **41**, 475; **48**, 368–372.
[5] Z. physik. Chem., **66**, 733.

centration. As a matter of fact, the temperature coefficients of the hydrolysis of imido ester salts[1] and acetamide[2] are only normal in magnitude when the active mass of the ionized portion of the water is left out of consideration altogether. The corresponding temperature coefficient for cane sugar[3] is rather large, although part of this may be due to changes in viscosity and to other abnormal physical properties which Morse and Frazer[4] showed prevent the strict application of the laws for ideal solutions. It may well be, then, that cane sugar reacts partly with the molecular water and partly with the hydroxyl and hydrogen ions together. More data for very dilute solutions of cane sugar would help us to ascertain the influence that viscosity exercises on the reaction velocities. Similar data for the hydrolysis of esters by acids would be very helpful.

We can all agree, then, that the "salt effect" is a very complicated phenomenon varying in nature in different cases, of which the true underlying principles can be learned only by the very accurate data now being collected by the different workers. In his study of the catalytic action of ethylates on the addition of alcohol to *p*-bromobenzonitrile Dr. C. N. Myers has found that there is apparently no "abnormal salt effect" noticed in the dilute solutions (N/32 to N/2048), this factor becoming measurable only in the more concentrated solutions (N/8 to N/32). We are now especially attempting to use the electron theory[5] to guide us in correlating our data and predicting other relationships. *We do not believe that chemists have yet discovered the fundamental laws which explain "how and why" chemical reactions take place. The idea that both ions and non-ionized compounds react is therefore presented only tentatively, as are all theories, pending the final reports.*

EXPERIMENTAL

Sodium Salt of 1-Phenylthiourazole.—The phenylthiourazole was made in the way described by Shadinger, and was recrys-

[1] Derby: This Journal, **39**, 470–1.
[2] Ostwald: J. prakt. Chem., [2] **27**, 25. Crocker: J. Chem. Soc., **91**, 603.
[3] J. Spohr: J. prakt. Chem., [2] **32**, 32. Euler: Z. physik. Chem., **32**, 348.
[4] This Journal, **34**, 28; **48**, 29.
[5] Acree: This Journal, **48**, 372.

tallized quickly from hot alcohol until it melted sharply at 195°. This acid was then titrated with the exact equivalent of sodium bicarbonate in a hot solution and the solution was evaporated to a small volume. The sodium salt crystallizes well with 3 molecules of water of crystallization. As only one molecule of water, approximately, is removed at 110°, and a small amount of decomposition was noticed, the hydrated salt was crystallized several times from alcohol and used for all the work. The theoretical amount of water in this salt is 20.07 per cent.; an analysis of one sample by the sodium sulphate method gave 20.28 per cent., and analyses of two other samples by the iodine method (see below) gave 19.68 and 20.02 per cent., respectively.

Absolute Ethyl Alcohol.—This solvent was prepared from commercial 95 per cent. alcohol which was boiled with lime two days, distilled, allowed to stand over lime four days and distilled again, and then fractionated carefully. The alcohol contained probably not over 0.05 per cent. of water. A portion was obtained whose boiling point did not vary more than 0°.05, and whose conductivity ranged from 0.22×10^{-6} to 0.27×10^{-6}; this was used in the conductivity work. The remainder of the alcohol, which had a conductivity of 0.46×10^{-6}, was used in the reaction velocities. The ethyl iodide was carefully purified.

Conductivity Apparatus.—The bridge wire, resistance box and cells were very carefully calibrated just before the work was begun. The cells were sufficiently constant in resistance when 0.02 N potassium chloride solutions were used to standardize them; the molecular conductivity of this solution was assumed to be 129.8.

Analytical Methods.—The standard solutions of iodine and sodium thiosulphate were checked carefully against weighed portions of pure iodine and pure 1-phenyl-3-thiourazole neutralized exactly with an alkali in the presence of phenolphthalein.

The solutions of the sodium thiourazole were first made separately at 25°. Ten cc. of the urazole solution were pipetted

into 50 cc. water and titrated with the standard solution of iodine to determine the value of A', starch being added toward the end of the titration. The reaction takes place quantitatively as follows:

$$2C_6H_5N_3C_2OHSNa + I_2 \longrightarrow 2NaI + (C_6H_5N_3C_2OHS)_2$$

The solution of the ethyl iodide was then made at 25°, exactly equivalent to the solution of the urazole salt. Ten cc. portions of the urazole solution were pipetted into 20 cc. flasks and 10 cc. portions of the ethyl iodide solution carefully pipetted into these, both solutions being initially at 25°. At various intervals of time, t, the contents of the flasks were poured into 50 cc. of water, and the concentration of the urazole salt, $(A' - x)$, was determined by titration with the standard solution of iodine.

When the concentration, A', of the solution of the sodium thiourazole was not exactly that desired the proper correction was made in K_V, as can be seen in the tables. From the corrected value A, K_V and K_n were calculated according to Equation (*a*) in the introduction. The values of K_i and K_m were calculated from the series of simultaneous equations,

$$\begin{aligned} K_n &= K_i\alpha + K_m(1 - \alpha) \\ K'_n &= K_i\alpha' + K_m(1 - \alpha') \\ K''_n &= K_i\alpha'' + K_m(1 - \alpha''), \text{ etc.} \end{aligned}$$

and these are given in Table VIII. The values of K_i and K_m are quite constant, whereas the integral of Equation (*b*) leads to values of K_i and K_m that are not at all constant.

Table I.—0.3 N Sodium 1-Phenyl-3-thiourazole + 0.3 N Ethyl Iodide

t	A'	$A' - x$	x	$K'V$
10	53.08	30.92	22.16	0.0716
15	53.08	25.65	27.43	0.0713
20	53.08	22.26	30.82	0.0692
25	53.08	19.46	33.62	0.0691
30	53.08	17.49	35.59	0.0678
40	53.08	14.40	38.68	0.0671

$A = 52.54$, $K_V = 0.0687$, $K_n = 0.229$ Mean, 0.0694

Table II.—0.2 N Sodium 1-Phenyl-3-thiourazole + 0.2 N Ethyl Iodide

t	A'	$A'-x$	x	$K'V$
10	34.94	22.88	12.06	0.0527
15	34.94	19.63	15.31	0.0520
20	34.94	17.03	17.91	0.0526
25	34.94	14.96	19.98	0.0534
35	34.94	12.45	22.49	0.0516
60	34.94	8.45	26.49	0.0522

$A = 35.03$, $K_V = 0.0524$, $K_n = 0.262$ Mean, 0.0524

Table III.—0.1 N Sodium 1-Phenyl-3-thiourazole + 0.1 N Ethyl Iodide

t	A'	$A'-x$	x	$K'V$
15	17.47	12.19	5.28	0.0288
25	17.47	10.23	7.24	0.0283
35	17.47	8.85	8.62	0.0278
45	17.47	7.71	9.76	0.0281
60	17.47	6.28	11.19	0.0296
90	17.47	5.10	12.37	0.0269

$A = 17.51$, $K_V = 0.0283$, $K_n = 0.283$ Mean, 0.0283

Table IV.—0.05 N Sodium 1-Phenyl-3-thiourazole + 0.05 N Ethyl Iodide

t	A'	$A'-x$	x	$K'V$
20	8.74	6.55	2.19	0.0167
30	8.74	6.07	2.67	0.0146
45	8.74	5.16	3.58	0.0154
60	8.74	4.50	4.24	0.0157
90	8.74	3.73	5.01	0.0149
120	8.74	3.14	5.60	0.0148

$A = 8.76$, $K_V = 0.0154$, $K_n = 0.308$ Mean, 0.0154

Table V.—0.025 N Sodium 1-Phenyl-3-thiourazole + 0.025 N Ethyl Iodide

t	A'	$A'-x$	x	$K'V$
30	4.23	3.45	0.78	0.0078
60	4.23	2.88	1.35	0.0078
90	4.23	2.61	1.62	0.0069
120	4.23	2.23	2.00	0.0075
210	4.23	1.51	2.72	0.0085
300	4.23	1.26	2.97	0.0079

$A = 4.38$, $K^V = 0.0080$, $K_n = 0.320$ Mean, 0.0077

Table VI

V	3.33	5.0	10.0	20.0	40.0
K_n	0.229	0.262	0.283	0.308	0.320

Table VII.—Conductivities of the Sodium Salt of 1-Phenyl-3-thiourazole in Ethyl Alcohol at 25°

V	μ_v (1)	μ_v (2)	α (1)	α (2)	$1-\alpha$ (1)	$1-\alpha$ (2)
3.33	9.08	9.23	27.25	27.7	72.75	72.3
5.0	10.79	10.88	32.4	32.6	67.6	67.4
6.67	12.09	...	36.3	....	63.7	....
10.0	14.04	14.26	42.1	42.7	57.9	47.3
20.0	17.61	17.44	52.8	52.4	47.2	47.6
40.0	19.11	19.49	57.3	58.5	42.7	41.5

$\mu_\infty = 33.3$

Table VIII

	K_i (1)	K_i (2)	K_m (1)	K_m (2)
V = 3.33 : 10	0.49	0.48	0.14	0.13
V = 3.33 : 20	0.45	0.46	0.15	0.14
V = 3.33 : 40	0.45	0.44	0.15	0.15
V = 5 : 10	0.41	0.40	0.19	0.19
V = 5 : 20	0.41	0.42	0.19	0.19
V = 5 : 40	0.42	0.41	0.185	0.19
V = 10 : 20	0.42	0.44	0.185	(0.27)
V = 10 : 40	0.42	0.42	0.180	0.18
V = 20 : 40	0.45	0.40	0.17	0.20
Average,	0.435	0.43 Av.	0.17	0.17

$K_i : K_m = 2.5$

SUMMARY

(1) The velocity of the reaction of ethyl iodide and sodium 1-phenyl-3-thiourazole has been measured in solutions varying from 0.3 N to 0.025 N. The per cent. of ionization of the sodium salt was measured at the same concentrations by the conductivity method.

(2) The data obtained were substituted in the equation $K_n = K_i\alpha + K_m\ (1-\alpha)$, and satisfactory constants were obtained for K_i and K_m. The conclusion is that the reaction velocity is, in this case, a function of the concentrations of

both the urazole ions and the nonionized urazole salt. While this conclusion is presented only tentatively pending our final report, a large amount of data secured from work with ethylates, phenolates, nitriles and other compounds harmonizes with this point of view. The influence of *auto* and other "salt effects" will be discussed in the completed articles.

JOHNS HOPKINS UNIVERSITY
May 1, 1908

ON THE REVERSIBLE ADDITION OF ALCOHOLS TO NITRILES CATALYZED BY ETHYLATES. I

BY E. K. MARSHALL, JR., AND S. F. ACREE

[FOURTEENTH[1] COMMUNICATION ON CATALYSIS]

(We are indebted to the Carnegie Institution of Washington for aid in these researches.)

In connection with the studies of catalysis carried on in this laboratory we have undertaken a series of investigations dealing with the chemical action of the ethylates of sodium, potassium, lithium, thallium and other metals in absolute ethyl alcohol on various organic compounds. E. K. Marshall, Jr., H. C. Robertson, Jr., J. H. Shrader, Miss B. M. Brown and Dr. Julia P. Harrison have found that sodium, potassium and lithium ethylates react with alkyl halides and form ethers and sodium halides by bimolecular reactions which seem to involve *both the ethylate ions*[2] *and the nonionized ethylate salt.*[3]

$$C_2H_5ONa + IC_2H_5 \longrightarrow (C_2H_5)_2O + \overset{+}{Na} + \overline{I}$$

$$C_2H_5\overline{O} + IC_2H_5 \longrightarrow (C_2H_5)_2O + \overline{I}$$

Robertson and Shrader[4] showed that sodium, potassium and lithium phenolates react with alkyl halides and form phenol ethers in exactly the same way, *both the nonionized phenolate salts and the phenolate ions apparently reacting with the alkyl*

[1] THIS JOURNAL, **27**, 118; **28**, 370; **31**, 185; **32**, 606; **37**, 71, 361; **38**, 1, 258, 489, 746; **39**, 124, 145, 226, 300; **41**, 457, 483; **42**, 115; **43**, 358, 505; **44**, 219; **48**, 352; **49**, 116. Ber. d. chem. Ges., **33**, 1520; **35**, 553; **36**, 3139; **37**, 184, 618; **41**, 3199. Science, **30**, 617 (1909). J. Am. Chem. Soc., **30**, 1755.

[2] For references to the work of Bredig, Lapworth, Goldschmidt, Euler, Acree, and Stieglitz, see THIS JOURNAL, **38**, 258; **48**, 352.

[3] See especially THIS JOURNAL, **48**, 353, 378.

[4] *Ibid.*, **48**, 357, 378.

halide. F. M. Rogers, Sidney Nirdlinger[1] and J. Chandler have shown that *ethyl iodide reacts with the nonionized sodium salt of 1-phenyl-3-thiourazole, as well as with the urazole anion.* The conductivity and ionization of all these salts have been measured by H. C. Robertson, Jr., in solutions varying in concentration from N/1 to N/16000, and the velocity of the reactions was measured in solutions varying from N/1 to N/32 or N/64. The "normal"[2] and "abnormal" "salt effects" have been measured by adding known quantities of sodium iodide, sodium bromide, potassium iodide and potassium bromide to these solutions, the ionization of the separate salts and of the mixtures having been accurately measured by Dr. Robertson. The details of all these investigations will appear in due time, after such physical factors as viscosity, solvation, double compounds and electronic phenomena have been investigated more fully.

It will be observed, however, that in all of these reactions the ethylate, phenolate and urazole salt are transformed into the end product, these being cases of "pseudo catalysis." We have therefore desired to study a number of cases in which the ethylate salts bring about their transformations "purely catalytically" and are not appreciably used up in the process, such studies being very desirable in order to learn whether the mechanism of the reaction of the ethylate is the same in "pure catalysis"[3] as in "pseudo catalysis" and involves both the ethylate ions and the nonionized ethylate salts. Such a case of "pure catalysis" has been worked out beautifully by Tubandt[4] in his investigation of the reversible inversion of *d*- and *l*-menthone by sodium ethylate, and we have shown[5] that his data give excellent evidence that *both the ethylate ions and the nonionized sodium ethylate are equally active in the inversion of the menthone.*

[1] This Journal, **48**, 358, 378; **49**, 116.

[2] The "normal salt effect" is the change in the velocity of transformation of the active salt resulting from the variation in ionization accompanying changes in its concentration on the addition of another salt. We call any *additional* change in reaction velocity an "abnormal salt effect."

[3] See This Journal, **48**, 362, and earlier papers for a full discussion of this subject.

[4] Ann. Chem. (Liebig), **339**, 41; **354**, 259; **377**, 284.

[5] This Journal, **48**, 359.

We have wished to take up other cases of such reversible reactions to learn whether the two opposing reactions are accelerated to the same extent by the ethylate ions and the nonionized ethylate salts; in other words, to learn whether the ratio $K_i : K_m$ is the same for the opposing reactions. In continuation of the reaction of hydroxylamine with carbonyl compounds,[1] which is accelerated by ethylates, Dr. E. K. Marshall, Jr., is studying the addition of ammonia and its substitution products, hydroxylamine, etc., to unsaturated compounds and in particular the reversible reaction,

$$RN:CS + R'NH_2 \rightleftarrows RNHCSNHR'$$

In general, the reaction goes too far toward the right to be studied accurately *from both sides* as a reversible reaction, and Dr. Marshall has found that *the velocity is not changed by the addition of ethylates, ammonium bromide or ammonium iodide.* This shows that the amines do not react with the mustard oils through their amide ions alone, $\overline{NH}_2$,

$$\overset{+}{Na} + \overline{O}C_2H_5 + NH_3 \leftrightarrows \overset{+}{Na} + \overline{NH}_2 + HOC_2H_5$$

$$2NH_3 \rightleftarrows \overset{+}{NH}_4 + \overline{NH}_2$$

but rather as NH_3 or possibly *both* its ions, a result also in harmony with our data on the reaction of ammonia with ethyl formate,

$$(HCOOC_2H_5 + NH_3 \rightleftarrows HCOOC_2H_5.\overset{+}{H} + \overline{NH}_2) \longrightarrow HCONH_2 + C_2H_5OH$$

as against

$$(HCOOC_2H_5 + \overset{+}{NH}_4 \rightleftarrows HCOOC_2H_5 + \overset{+}{H} + NH_3 \rightleftarrows HCOOC_2H_5.\overset{+}{H} + NH_3) \longrightarrow HCONH_2 + \overset{+}{H} + C_2H_5OH$$

the velocity of which is not appreciably changed by the addition of ammonium chloride.[2] The details of this work will appear shortly.

Another class of reactions which we have undertaken to study are those involving the reversible (or irreversible) addition of alco-

[1] THIS JOURNAL, **38**, 308; **39**, 300. Desha: Diss., Johns Hopkins Univ., 1907.

[2] See also Stieglitz: J. Am. Chem. Soc., **32**, 230.

hols to unsaturated compounds, especially those catalyzed by ethylates.[1] Dr. Marshall has begun to investigate the reversible addition of alcohol to mustard oils, a transformation which is enormously accelerated by ethylates.[2] Another similar case which should be investigated is the addition of alcohols to olefins, such as acrylic, crotonic, maleic and fumaric esters,[3] a reaction generally proceeding too slowly to be detected except when catalyzed by ethylates. Friedländer[4] and Mähly found, however, that the compounds *m*- and *p*-$NO_2C_6H_4CH : C(NO_2)COOCH_3$ and the ethyl esters add methyl alcohol and ethyl alcohol without the aid of ethylates, and yield such products as

$$NO_2C_6H_4CH(OC_2H_5)CH(NO_2)COOCH_3$$

An excellent reaction for study in this connection is the reversible addition of alcohols to nitriles, catalyzed by ethylates and methylates. The nitriles studied by us do not add alcohols with any appreciable velocity unless catalyzed by acids or ethylates, as special experiments have uniformly shown. The idea that all nitriles may add alcohol in the presence of ethylates is merely an extension of the work of Purdie[5] on the fumaric and maleic acid esters, of Wurtz,[5] Hofmann,[5] Schiff,[5] and others, on the isocyanates and mustard oils, of Kremann,[6] Claisen,[7] Kossel,[8] and others, on esterifications by ethylates,

$$C_6H_5COOCH_3 + NaOC_2H_5 \longrightarrow C_6H_5COOC_2H_5 + NaOCH_3$$

of Stieglitz[9] and Dains on the carbodiimides, and especially of Nef on the nitriles,[10] and of Stieglitz[11] and McKee, and of

[1] Professor Stieglitz has written me that he too has for several years believed that the activity of the ethylates in all such reactions would be found to depend upon the "electrical conditions" of the solutions.

[2] Hofmann: Ber. d. chem. Ges., **2**, 120; **3**, 772. Bamberger: *Ibid.*, **15**, 2164. Schiff: *Ibid.*, **9**, 1316. Wurtz: Ann. chim phys., [3] **42**, 43.

[3] Purdie: J. Chem. Soc., **39**, 344; **47**, 863, 867; **59**, 469.

[4] Ann. Chem. (Liebig), **229**, 210.

[5] *Loc. cit.*

[6] Kremann: Monats. Chem., **26**, 783; **29**, 23.

[7] Claisen: Ber. d. chem. Ges., **20**, 646.

[8] Kossel, Krüger and Obermüller: Z. physiol. Chem., **15**, 321; **16**, 153.

[9] Dains: J. Am. Chem. Soc., **21**, 136.

[10] Nef: Ann. Chem. (Liebig), **287**, 280.

[11] McKee: This Journal, **26**, 206.

McKee,[1] on the addition of alcohols to cyanoamides in the presence of the corresponding alcoholates:

$$R_2NCN + HOC_2H_5 \longrightarrow R_2NC(:NH)OC_2H_5$$

We have never seen a statement that the reverse reaction, the decomposition of an imido ester into the nitrile and the alcohol, takes place in alcohol in the presence of ethylates, although imido esters are decomposed in this way in water by alkalies.[2] It was this general parallelism in the reactivity of sodium ethylate and sodium hydroxide that made us suspect that sodium ethylate would cause imido esters to decompose into nitriles and alcohols.

In every case examined we have found the reaction to be reversible. The equilibrium point is the same whether measured from the nitrile or the imido ester, although slow disturbing side reactions make the agreement in some cases less satisfactory than desired. The equilibrium point varies very widely with the different compounds. The per cent. of imido ester formed is illustrated by the following examples: butyronitrile, 0.90; propionitrile, 1.75; acetonitrile, 2.50; *p*-tolunitrile, 6.8; benzonitrile, 14.0; *p*-bromobenzonitrile, 27.2; *m*-bromobenzonitrile, 38.0; *p*-nitrobenzonitrile, 62.0; *m*-nitrobenzonitrile, 78.0; diisoamylcyanoamide, 98.0. The equilibrium point varies rather widely in some cases with changes in the concentrations of the nitrile and the ethylate, but fluctuates very little in other examples. Different ethylates catalyze the reaction with different velocities and the equilibrium points also often vary in such cases. The velocity of the reaction varies greatly with the different nitriles, the *p*-nitrobenzonitrile reacting very rapidly, whereas *o*-tolunitrile hardly adds alcohol at all.

Stieglitz and Schlesinger[3] found that barium hydroxide causes the decomposition of imido esters *in water* into nitriles and alcohols, and they interpreted their results on the Ostwald-Arrhenius hypothesis that the decomposition is due to the hydroxyl ions *alone*, as in the case of the saponification

[1] McKee: This Journal, **36**, 209; **42**, 1.

[2] See especially a fine study by Stieglitz and Schlesinger: This Journal, **39**, 738.

[3] Stieglitz and Schlesinger: This Journal, **39**, 738.

of ordinary esters by hydroxides. But we[1] have recalculated their excellent data and have found that the concentration of the barium hydroxide molecules is so small, about three to seven per cent., that *their results can be reinterpreted fully as well on our theory that both the hydroxyl ions and the nonionized barium hydroxide are, in this case, equally active.* Our theory, then, applies equally well to their work and to ours, whereas their[2] theory that only the hydroxyl ions (or the ethylate ions, in our case) are active does not at all agree with our work on the ethylates, as the following discussion will show.

Having learned that the reaction is reversible, we have begun the quantitative study of several cases to learn whether the ethylate ions and the nonionized sodium, potassium, and lithium ethylates catalyze both of the reverse reactions exactly alike; that is, whether the ratio $K_i : K_m$ is the same for the opposing reactions. Dr. E. K. Marshall has learned that sodium ethylate, in concentrations varying from N/4 to N/64, causes the decomposition of N/4 acetimido ethyl ester with the velocities $K_i = 0.344$ and $K_m = 0.228$. Dr. Julia P. Harrison showed that sodium ethylate, in concentrations varying from N/4 to N/64, causes the decomposition of N/4 benzimido ethyl ester with the velocities $K_i = 0.1148$ and $K_m = 0.1003$. Dr. Marshall and Dr. Harrison have shown that added sodium iodide lowers the per cent. of ionization and the reaction velocity "normally," or to just the extent calculated from our theory. Dr. C. N. Myers has studied the reversible addition of ethyl alcohol to 0.15 N *p*-bromobenzonitrile in the presence of sodium ethylate varying in concentration from N/8 to N/2048 N and has found that the ethylate ions and the nonionized sodium ethylate are about equally active and act purely catalytically. Of especial importance is the fact that there is no "abnormal salt effect" by the ethylate noticed in the very dilute solutions

[1] Acree: This Journal, **48**, 359.

[2] Stieglitz now finds (J. Am. Chem. Soc., **34**, 1689, 1690, 1694) that he can reinterpret both the imido ester work and the Beckmann rearrangement as *reactions of both ions and nonionized* salts, augmented by a salt catalysis proportional to the concentration of the total salt present. We had pointed out 4 years ago that the nonionized imido ester salts should be considered (This Journal, **39**, 521; and especially *Ibid.*, **48**, 368).

(N/32 to N/2048), this factor becoming appreciable only in the more concentrated solutions (N/8 to N/32). In these *ideal* solutions the value for K_i for the *ethylate ion* is the same for both sodium ethylate and lithium ethylate, but the values for K_m for the *nonionized* sodium ethylate and lithium ethylate are considerably different, in accordance with our theory. We consider this work on the *p*-bromobenzonitrile to be our first *complete proof* of the *simultaneous activity of ions and non-ionized* salts, because these *ideal* solutions are free from the abnormal physical properties which make the interpretation of the data for concentrated solutions less rigorous. All of these investigations will be published in due time when the action of sodium, potassium and lithium ethylates on several nitriles, and the reverse reactions, have been studied in widely varying concentrations, in the presence of different amounts of added salts and at different temperatures. The effect of certain physical factors will be especially investigated.

EXPERIMENTAL

The bath used in this work was a large one, which has been used for some time in this laboratory in investigations on reaction velocities and will be fully described elsewhere. Its temperature was constant at 25° to within ±0°.005.

The *absolute alcohol* was prepared by distillation from lime. The amount of water remaining in the alcohol was never more than 0.03 per cent. Generally, it contained considerably less than this, as was determined by careful specific gravity estimations. The solutions of sodium ethylate were prepared very carefully by a method which will be described in the work on the "Reactions between Sodium Ethylate and Alkyl Halides," soon to be published. The solutions of the nitriles were prepared by weighing into a flask containing alcohol a little more than the required amount, diluting to the mark, and then measuring in sufficient alcohol to bring the solution to the required normality. The solutions of the imido esters were prepared by mixing a standard solution of the imido ester hydrochloride with a sodium ethylate solution of such a concentration that the resulting mixture contained the proper proportions of the two reacting constituents. The sodium

chloride, precipitated out in the above procedure, was allowed to remain in the bottom of the flask, as check experiments with the free benzimido ethyl ester showed that the salt produced no abnormal effect. The titrations were carried out with standard hydrochloric acid and methyl orange but were not very sharp except in the case of the aliphatic imido esters. The aromatic imido ester hydrochlorides are more or less hydrolyzed, while the aliphatic ones, being stronger bases, are much less affected.

In all of the following tables we give the volume of acid necessary to neutralize *both* the ethylate and the imido ester. By subtracting the amount of acid corresponding to the concentration of the ethylate we find the volume of acid necessary to neutralize the imido ester; when this volume is divided by the volume corresponding to a theoretical yield of imido ester (or nitrile) we obtain the "per cent. of imido ester at equilibrium," which is given at the bottom of each table.

Benzonitrile and Benzimido Ethyl Ester

Benzonitrile was purified by redistillation. Its boiling point was constant to within 0°.5, 186°.5–187° (uncorr.).

Benzimido Ethyl Ester Hydrochloride.—This was prepared as described by Pinner,[1] by treating a mixture of one mole benzonitrile and 1.25 moles of alcohol with a little more than 1 mole of dry hydrochloric acid gas. Crystallization was started by adding some of the salt and the solution was allowed to stand at 0° in a well stoppered flask for two or three days, when the solid mass was broken up and washed with cold alcohol and ether. It was preserved in a vacuum desiccator over calcium oxide. It is soluble in alcohol only enough to give a solution a little stronger than half normal.

Benzimido ethyl ester was prepared only in small quantity. The method used was that described by Stieglitz.[2]

To confirm the quantitative data that the addition of alcohol to the benzonitrile takes place as described, a qualitative experiment was carried out as follows: Fifteen grams of benzonitrile dissolved in 75 cc. of alcohol were treated with 25 cc. of a normal solution of sodium ethylate, and the

[1] Die Imidoäther und ihre Derivate, Berlin, **1892**, p. 53.

[2] This Journal, **39**, 443.

mixture allowed to stand at 25° for 36 hours. It was then poured into a separating funnel containing 300 cc. of cold water, acidified, and extracted twice with ether. The ethereal solution contained the unchanged nitrile. The aqueous solution was made alkaline and again extracted with ether. The ethereal solution was dried several times over calcium chloride, filtered and treated with dry hydrochloric acid gas. One and three-tenths grams of a white substance were obtained, which resembled in all its properties the benzimido ethyl ester hydrochloride. It melted with decomposition at 124°–126°. The analysis showed that it was probably contaminated with ammonium chloride formed in its isolation.

Analysis: 0.5035 gram gave 0.4602 gram AgCl. Chlorine found, 22.53 per cent.; theoretical for the imido ester salt, 19.11 per cent.; theoretical for ammonium chloride, 66.28 per cent.

The ethereal extract from the acid solution was freed from ether by distillation, and the residue heated to 100° to dry it. Twelve grams of an oil were obtained which was shown by its odor and boiling point, 187°–188°, to be benzonitrile.

Table I.—0.25 N Benzonitrile with Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$[1]	0.75 N		0.25 N		0.125 N	
Vol. taken for each titration	10 cc.		10 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.1 N HCl	*t*	cc. 0.2 N HCl
	0 min.	37.50	0 min.	25.00	0 min.	12.50
	5.25 "	38.20	5.66 "	25.36	60 "	13.66
	11.5 "	38.44	14 "	25.68	120 "	14.28
	20.5 "	38.57	24 "	25.98	210 "	14.65
	45 "	38.61	36 "	26.36	22 hrs.	14.88
	106 "	38.66	22 hrs.	27.28	26 "	14.85
	24 hrs.	38.61	24 "	27.18		
	28 "	38.44	144 "	27.12		
	48 "	38.35				
	72 "	38.38				
Per cent. ester at equil.	9.28		9.12		9.52	

[1] *Equal* volumes of the nitrile or imido ester solution and the sodium ethylate were generally used. All the concentrations given in this paper refer to the solutions after mixing.

Table II.—0.25 N Benzimido Ethyl Ester with Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.75 N		0.25 N		0.125 N	
Vol. taken for each titration	10 cc.		10 cc.		10 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	50.00	0 min.	25.00	0 min.	18.75
	5 "	43.99	6 "	23.14	20 "	16.69
	15 "	40.70	∞	13.69	45 "	14.10
	25 "	39.21		13.71	89 "	11.35
	40 "	38.70			119 "	10.28
	55 "	38.65			179 "	8.53
	75 "	38.63			239 "	8.25
	∞	38.61			22 hrs.	7.43
					26 "	7.45
Per cent. ester at equil.	8.88		9.60		9.52	

The following table shows the results obtained with varying concentrations of sodium ethylate, the concentrations of the benzonitrile or imido ester being constant:

Table III

Conc. $NaOC_2H_5$	0.25 N benzonitrile Per cent. ester at equil.	0.25 N benzimido ethyl ester Per cent. ester at equil.
0.75 N	9.28	8.88
0.25 N	9.12	9.60
0.125 N	9.52	9.52

The equilibrium point remains constant within the limits of experimental error.

Table IV.—0.5 N Sodium Ethylate with Varying Concentrations of Benzonitrile

Conc. C_6H_5CN	0.5 N		0.5 N	
Vol. taken for each titration	10 cc.		10 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	25.00	0 min.	25.00
	20 "	26.34	5 "	25.65
	40 "	26.80	10 "	25.96
	70 "	26.88	15 "	26.19
	∞		25 "	26.57
		26.90	35 "	26.78
		26.89	57	26.86
			∞	26.93
Per cent. ester at equil.	7.60		7.72	

Conc. C_6H_5CN	0.25 N		0.375 N	
Vol. taken for each titration	10 cc.		10 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	25.00	0 min.	25.00
	15 "	25.66	7 "	25.58
	44 "	26.02	20 "	26.14
	67 "	26.12	30 "	26.36
	∞	26.11	∞	26.57
Per cent. ester at equil.	9.06		8.37	

Conc. C_6H_5CN	0.125 N		0.0625 N		0.03125 N	
Vol. taken for each titration	20 cc.		20 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	50.00	0 min.	50.00	0 min.	50.00
	∞	51.37	∞	50.91	∞	50.47
		51.41		50.90		50.40
		51.40		50.87		50.42
		51.38		50.89		50.46
Per cent. ester at equil.	11.12		14.08		14.10	

The following table is a collection of the above results, showing the change in the equilibrium point produced by a change in the concentration of the benzonitrile; N sodium ethylate was used in all cases:

Table V

Conc. benzonitrile after mixing	Per cent. imido ester present at equilibrium
0.5 N	7.60
0.5 N	7.72
0.375 N	8.37
0.25 N	9.06
0.125 N	11.12
0.0625 N	14.08
0.03125 N	14.10

The change in concentration of the alcohol due to its combination with the nitrile, and due to the preparation of solutions of different concentrations,[1] is not sufficient to account for this change in equilibrium with change of the concentration of the nitrile; that is, calculations on the basis of a reversible bimolecular-monomolecular reaction give practically the same equilibrium constants as those calculated on the basis of a reversible monomolecular reaction, assuming the concentration of the alcohol to be constant.

p-*Tolunitrile and* p-*Tolimido Ethyl Ester*

The *p*-tolunitrile was purified by extracting with acid, and then with alkali several times. It was then washed thoroughly with water and dried by standing several days in a vacuum desiccator over sulphuric acid. Difficulty is experienced in the titration of solutions containing this nitrile, as it separates out on addition of water, and obscures the color change of the indicator.

p-*Tolimido ethyl ester hydrochloride* was prepared as described by Pinner.[2] The purity of the compound was determined by precipitating the chlorine and weighing the silver chloride.

0.7698 gram substance gave 0.5593 gram AgCl. Theo-

[1] The solutions were prepared on a volume normal basis; therefore, the more concentrated the solution the less alcohol used in preparing it.

[2] *Loc. cit.*, page 61.

retical amount of chlorine, 17.85 per cent.; found, 17.77 per cent.

Table VI.—0.25 N p-*Tolunitrile and Varying Concentrations of Sodium Ethylate*

Conc. $NaOC_2H_5$	0.25 N		0.125 N	
Vol. taken for each titration	10 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	12.50	0 min.	12.46
	10 "	12.84	∞	14.16
	55 "	13.06		14.14
	115 "	13.18		
	175 "	13.35		
	∞	13.36		
Per cent. ester at equil.	6.80		6.71	

Table VII.—0.25 N p-*Tolimido Ethyl Ester and Sodium Ethylate*

Conc. $NaOC_2H_5$	0.25 N	
Vol. taken for each titration	10 cc.	
	t	cc. 0.2 N HCl
	0 min.	25.00
	10.5 "	22.84
	30.5 "	20.46
	50 "	18.08
	120 "	14.81
	200 "	13.65
	344 "	13.21
	∞	13.27
		13.25
Per cent. ester at equil.	6.08	

m-*Nitrobenzonitrile and* m-*Nitrobenzimido Ethyl Ester*

m-*Nitrobenzonitrile.*—This was made by the nitration of benzonitrile with potassium nitrate and sulphuric acid.[1] The crude product obtained was very impure, but was purified by precipitation from hot alcohol by the addition of water. When this process had been repeated three or four times the melting point remained constant at 115°.5–116°. The nitrile

[1] Schöpff: Ber. d. chem. Ges., **18**, 1063.

is not very readily soluble in cold alcohol, the strongest solution which could be obtained at 25° being eighth-normal.

m-*Nitrobenzimido Ethyl Ester Hydrochloride.*—This was prepared as described by Lossen.[1] Ten grams of the nitrile were dissolved in dry benzene, 3.2 grams alcohol added, and 2.46 grams dry hydrochloric acid gas passed in. The solution was allowed to stand for a week, and the precipitate filtered off. Thirteen grams were obtained.

Analysis: 0.7266 gram substance gave 0.4543 gram AgCl. Theoretical amount of chlorine, 15.38 per cent.; found, 15.45 per cent.

Table VIII.—0.0625 N m-*Nitrobenzonitrile and Varying Concentrations of Sodium Ethylate*

Conc. $NaOC_2H_5$	0.5 N		0.25 N	
Vol. taken for each titration	20 cc.		20 cc.	
	t	cc. 0.2 N HCl	t	cc. 0.2 N HCl
	0 min.	50.00	0 min.	25.00
	∞	54.92		29.88
		54.84	∞	30.00
				29.80
Per cent. ester at equil.	78.1		77.7	

Table IX.—0.0625 N m-*Nitrobenzimido Ethyl Ester and Varying Concentrations of Sodium Ethylate*

Conc. $NaOC_2H_5$	0.5 N		0.25 N	
Vol. taken for each titration	20 cc.		20 cc.	
	t	cc. 0.2 N HCl	t	cc. 0.2 N HCl
	0 min.	56.25	0 min.	31.25
	20 "	54.94	35 "	30.08
		54.93		29.76
	∞	54.83	∞	29.80
		54.85		29.83
Per cent. ester at equil.	78.2		76.8	

[1] Ann. Chem. (Liebig), **265**, 144

p-*Nitrobenzonitrile*

(By C. N. Myers).

This substance, which was bought from Hoffman and Kropff, melted at 145°. As the saturated solution at 25° is only 0.084 N, we have used 0.075 N solutions in all of the work. The experiments show that the alcohol and this nitrile react more rapidly than any other aromatic nitrile studied, the equilibrium being attained in about one hour. Portions were tested with *m*-phenylenediamine for sodium nitrite but no great color change was found. This shows that the sodium ethylate does not appreciably remove the nitro group from the benzene nucleus.

Table X.—0.05 N p-*Nitrobenzonitrile and Varying Concentrations of Sodium and Potassium Ethylate*

Conc. ethylate	0.03130 N $NaOC_2H_5$		0.08346 N KOC_2H_5	
Vol. taken for each titration	30 cc.		30 cc.	
	t	cc. 0.1 N HCl	*t*	cc. 0.1 N HCl
	23 min.	17.03	24 min.	33.12
	37 "	17.92	112 "	33.93
	57 "	18.63	187 "	33.97
	74 "	18.63	1260 "	34.30
	1340 "	18.48		
	2778 "	18.38	1300 "	34.28
Per cent. ester at equil.	61.6		61.6	

m-*Bromobenzonitrile and* m-*Bromobenzimido Ethyl Ester*

m-*Bromobenzonitrile* was prepared by Reid's[1] method of distilling the lead salt of *m*-bromobenzoic acid with lead sulphocyanate. It was purified by recrystallization from alcohol and melted at 38°–39°.

m-*Bromobenzimido Ethyl Ester Hydrochloride.*—No description of this compound could be found in the literature, although Stieglitz has used the compound in his investigations on "Catalysis of Imido Ethers."[2] It was prepared as follows: Eight grams of the nitrile were mixed with 2 grams alcohol,

[1] This Journal, **43**, 179.

[2] *Ibid.*, **39**, 609.

and enough dry ether added to bring the nitrile into solution. This was then treated with 1.7 grams dry hydrochloric acid gas, and allowed to stand. The solid which crystallized out was filtered and washed as usual with cold alcohol and ether. Only 2.5 grams were obtained, and no more substance would crystallize out on standing. On evaporation of the ether in a vacuum desiccator, 6.3 grams unchanged nitrile were obtained. This was mixed with 1.6 grams alcohol, and considerable more than the theoretical amount of hydrochloric acid gas passed in.

Three grams of imido ester hydrochloride were obtained.

Analysis: 0.3881 gram substance gave 0.2107 gram AgCl. Theoretical amount of chlorine, 13.40 per cent.; found, 13.42 per cent.

Owing to the difficulty experienced in obtaining this compound in satisfactory yield, it seemed advisable to test whether the reaction of the *m*-bromobenzonitrile, alcohol, and hydrochloric acid is reversible or not. Four-tenths gram portions of this imido ester hydrochloride were weighed out, dissolved in small flasks containing 20 cc. alcohol, and allowed to stand at 25° for different time periods. They were then taken out and titrated with standard sodium hydroxide and methyl orange. Owing to hydrolysis of the *m*-bromobenzimido ethyl ester hydrochloride, the titrations were not at all sharp, and no very definite end point could be determined; so the titrations were carried to approximately the same degree of intensity of the pink color.

Time in days	cc. 0.2 N NaOH
0	0.43
5	0.70
15	0.50
61	0.42

The solutions were then extracted with ether. No *m*-bromo nitrile was detected; its detection, however, would have been made difficult by the ethyl *m*-bromobenzoate formed by the action of the water on the imido ester hydrochloride. We may conclude, therefore, that this reaction, like that of the other ni-

triles with alcohol and hydrochloric acid, is practically non-reversible. That the other imido ester hydrochlorides do not change into nitrile, alcohol and hydrochloric acid was proven by allowing an alcoholic solution of the imido ester hydrochloride to stand. No more alkali was required for neutralization than that used in neutralizing the hydrochloric acid resulting from the hydrolysis of the imido ester hydrochloride.

Table XI.—0.125 N m-*Bromobenzonitrile and Varying Concentrations of Sodium Ethylate*

Conc. $NaOC_2H_5$	0.5 N		0.125 N	
Vol. taken for each titration	10 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	25.00	0 min.	12.50
	10 "	26.93	40 "	16.77
	31 "	27.25	∞	17.29, 17.34
	∞	27.35, 27.37, 27.37		
Per cent. ester at equil.	37.9		38.5	

Table XII.—0.125 N m-*Bromobenzimido Ethyl Ester and Sodium Ethylate*

Conc. $NaOC_2H_5$	0.5 N	
Vol. taken for each titration	10 cc.	
	t	cc. 0.2 N HCl
	0 min.	31.25
	13 "	27.44
	52 "	27.40
	170 "	27.32
	∞	27.35, 27.30
Per cent. ester at equil.	37.3	

p-*Bromobenzonitrile*

(By C. N. Myers)

The work with this substance, and with *p*-chlorobenzonitrile, *p*-nitrobenzonitrile, and *o*-bromo-*p*-methylbenzonitrile was done by Dr. C. N. Myers. The *p*-bromobenzonitrile was made by

the Sandmeyer reaction. It melted at 112°.5. The solubility is so small that 0.15 N solutions were used. The imido ester salt is hydrolyzed enough to make the titration somewhat uncertain. Dr. Myers has studied the reaction of 0.15 N *p*-bromobenzonitrile and sodium ethylate whose concentrations varied from N/8 to N/2048. The results show that the ethylate ions and the nonionized sodium ethylate are about equally effective in catalyzing the reaction. In calculating the reaction velocities, he used the formula

$$\frac{dx}{dt} = K_1 (A_1 - x) - K_2 x$$

or

$$K_v = K_1 + K_2 = \frac{KA_1}{KA_1 - (K+1)x}$$

in which A_1 is the original concentration of the nitrile, and x the concentration of the imido ester formed during the reaction. At equilibrium we have

$$K = \frac{K_1}{K_2} = \frac{x}{A_1 - x}$$

Table XIII.—0.15 N p-*Bromobenzonitrile and 0.00781 N Sodium Ethylate*

Ten cc. taken for each titration

A_1 = 30 cc. K = 0.373

t	x[1]	K_v	t	x[1]	K_v
72 min.	1.53	0.00124	48 min.	1.05	0.00125
102 "	2.07	0.00125	58 "	1.24	0.00124
134 "	2.62	0.00126	99 "	2.04	0.00126
174 "	3.28	0.00129	118 "	2.36	0.00126
259 "	4.26	0.00121	170 "	3.14	0.00124
277 "	4.43	0.00123	233 "	3.89	0.00121
312 "	4.72	0.00121			
	Ave.,	0.00124		Ave.,	0.00124
Per cent. ester at equil.		27.17			27.17

[1] See footnote p. 145.

Table XIV.—0.15 N p-*Bromobenzonitrile and 0.0039 N Sodium Ethylate*

Ten cc. taken for each titration

A_1 = 30 cc. K = 0.373

t	x[1]	K_v	t	x[1]	K_v
92 min.	1.04	0.000644	104 min.	1.14	0.000629
150 "	1.62	0.000638	128 "	1.39	0.000634
231 "	2.37	0.000646	178 "	1.86	0.000632
290 "	2.81	0.000633	208 "	2.12	0.000629
326 "	3 14	0.000648	312 "	3.01	0.000640
			377 "	3.45	0.000634
	Ave.,	0.000642		Ave.,	0.000633
Per cent. ester at equil.		27.17			27.17

p-*Chlorobenzonitrile*

(By C. N. Myers)

This compound was bought from Hoffman and Kropff. It melted at 92°.

Table XV.—0.1 N p-*Chlorobenzonitrile and 0.06255 N Sodium Ethylate*

Conc. $NaOC_2H_5$ 0.06255 N

Vol. taken for each titration 10 cc.

t	cc. 0.1 N HCl
249 min.	17.36
1010 "	17.42
1347 "	17.64
2495 "	17.65
3995 "	17.67

Per cent. ester at equil. 25.85

o-*Bromo*-p-*methylbenzonitrile*

(By C. N. Myers)

We have carried out a few experiments with this substance and with *o*-tolunitrile to learn whether the so-called space interference prevents the reaction of these nitriles with the alcohol. As was predicted, the reaction is so slow that practically no imido ester is formed even in five months.

[1] In these four tables we have called x the number of cc. of 0.1 N hydrochloric acid required to neutralize the imido ester formed.

Table XVI.—0.25 N o-*Bromo*-p-*methylbenzonitrile and 0.25 N Sodium Ethylate*

t	Cc. 0.1 N acid	Original titration	Cc. change
30 min.	25.00	25.02	—0.02
1400 "	25.02	25.03	—0.01
150 days	24.70	25.00	—0.30
150 "	24.74	25.00	—0.26

No precipitate was obtained when silver nitrate was added. Nitric acid was used in these titrations. Check experiments on the ethylate solutions show that small disturbing side reactions take place which, however, do not change the conclusion that the nitrile hardly reacts with the alcohol

Acetonitrile and Acetimido Ethyl Ester

Acetonitrile was purified by repeated distillation over phosphorus pentoxide and then alone.

Acetimido Ethyl Ester Hydrochloride.—Owing to the much greater reactivity of the aliphatic imid. ester hydrochlorides with alcohol to form ortho esters and ammonium chloride, and with water to form ethyl acetate and ammonium chloride, their preparation is usually accompanied with the formation of more or less ammonium chloride. If, according to the method described by Pinner,[1] the mixture of nitrile, alcohol and hydrochloric acid is allowed to stand until the hydrochloride crystallizes out, a pure preparation cannot be obtained; it is contaminated with more or less ammonium chloride. The following procedure gives a quantitative yield of very pure substance: Fifteen grams of acetonitrile and 17 grams alcohol cooled with ice were treated with 13 grams of dry hydrochloric acid gas. The sides of the flask were rubbed with a glass rod to induce crystallization from the viscous mass. After standing in the cold for 5 hours the whole contents of the flask had solidified to a hard crystalline mass which often could be removed only by breaking the flask. The mixture was allowed to stand packed in ice overnight (about

[1] *Loc. cit.*, page 27.

14 hours),[1] and was taken out, powdered, and washed 2 or 3 times with dry ether. Yield, 45 grams (theoretical yield, 45.2 grams).

Analysis: 0.9724 gram of substance gave 1.1302 gram AgCl. Chlorine: found, 28.76 per cent.; theoretical, 28.69 per cent.

The rapid decomposition of the imido ester hydrochloride into ammonium chloride in the course of the usual method of preparation is shown in the following experiment: Fifteen grams of acetonitrile, 17 grams alcohol, and 13 grams dry hydrochloric acid were allowed to stand overnight packed in ice. In the morning, on rubbing the sides of the flask, some of the substance crystallized out. This was filtered off immediately and washed with dry ether; yield, 23 grams (Sample *A*). The filtrate and washings were allowed to stand overnight and the precipitate filtered off; yield, 13.5 grams (Sample *B*). The filtrate from this was allowed to stand for four days and then the precipitate filtered off; yield, 3 grams (Sample *C*). From this filtrate, a week later, a fourth fraction was obtained (Sample *D*), 0.4 gram. Each sample was dried in a vacuum desiccator over burnt lime before analysis.

Analysis of Sample *A*:

1.1135 grams substance gave 1.2954 grams AgCl. Found chlorine, 28.77 per cent. 0.2000 gram substance required 16.23 cc. 0.1 N $AgNO_3$. Found chlorine, 28.77 per cent. 0.3662 gram required 29.82 cc. 0.1 N $AgNO_3$. Found chlorine, 28.87 per cent. Theoretical chlorine, 28.69 per cent.

Analysis of Sample *B*:

0.5804 gram substance required 49.91 cc. 0.1 N $AgNO_3$; found chlorine, 30.41 per cent.

0.4120 gram substance required 35.36 cc. 0.1 N $AgNO_3$; found chlorine, 30.43 per cent.

Analysis of Sample *C*:

0.1778 gram substance required 32.82 cc. 0.1 N $AgNO_3$; found chlorine, 65.47 per cent.

Analysis of Sample *D*:

[1] In later experiments, crystals of the pure acetimidoethyl ester hydrochloride were added after the mixture had stood in ice a couple of hours. In the morning the whole contents of the flask had crystallized out in characteristic large crystals, and could be filtered off immediately.

0.3656 gram substance required 67.71 cc. 0.1 N $AgNO_3$; found chlorine, 65.68 per cent. Theoretical chlorine for NH_4Cl, 66.28 per cent.

The fact that the samples, when dissolved in water, did not give any acidity, and that after standing one or two days in a vacuum desiccator over burnt lime, the chlorine content did not change, shows that there was no free hydrochloric acid occluded in the precipitate.

That the pure acetimido ethyl ester hydrochloride can be kept without appreciable decomposition is shown by the following data:

1. Analysis of a sample gave 28.76 per cent. chlorine. Same sample 20 days later gave 28.76 per cent. chlorine.

2. Analysis of a sample gave 28.77 per cent. chlorine. Same sample 6 days later gave 28.80 per cent. chlorine.

Decomposition of the Acetimido Ethyl Ester Hydrochloride into Acetamide and Ethyl Chloride

This decomposition, which takes place very rapidly when the substance is heated to its melting point, was found to take place slowly in alcoholic solution at 25°. Weighed amounts of the imido ester hydrochloride were dissolved in small flasks in 20 cc. alcohol and allowed to stand at 25° for different time periods. They were then taken out, poured into water, and the chlorine determined. Ammonium chloride crystallized out in the flasks, owing to the reaction between the imido ester hydrochloride and alcohol to form ortho ester and ammonium chloride. The following table shows the gradual loss of chlorine due to the above decomposition and escape of ethyl chloride:

Time (hours)	Wt. hydrochloride taken	Wt. AgCl obtained	Per cent. chlorine
0.50	1.1251	1.3040	28.67
2.50	1.2080	1.3948	28.56
48.0	1.2914	1.4793	28.33
150.0	1.2355	1.3822	27.73

The acetimido ester hydrochloride used in the above experiments contained 28.76 per cent. chlorine. The acetamide was not isolated.

Table XVII.—0.25 N Acetonitrile and Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.5 N		0.25 N	
Vol. taken for each titration	10 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	25.00	0 min.	25.00
	5 "	25.20		
	37 "	25.21	∞	25.46
	∞	25.20		25.44
		25.22		
Per cent. ester at equil.	1.68		1.80	

Conc. $NaOC_2H_5$	0.125 N		0.0625 N	
Vol. taken for each titration	20 cc.		20 cc.	
	t	cc. 0.2 N HCl.	*t*	cc. 0.2 N HCl
	0 min.	12.50	0 min.	6.25
	∞	12.92	∞	6.64
		12.90		6.65
				6.65
Per cent. ester at equil.	1.64		1.80	

Table XVIII.—Varying Concentrations of Acetonitrile and Sodium Ethylate

Conc. $NaOC_2H_5$	0.5 N		0.25 N		0.25 N	
Conc. nitrile	0.5 N		0.125 N		0.0625 N	
Vol. taken for each titration	10 cc.		20 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	25.00	0 min.	24.68	0 min.	24.97
	∞	25.36	∞	24.98	∞	25.12
		25.35		25.00		25.14
		25.35				25.13
		25.38				
Per cent. ester at equil.	1.44		2.48		2.56	

Table XIX.—0.25 N Acetonitrile and Varying Concentrations of Potassium Ethylate

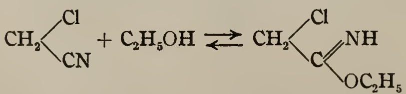
Conc. KOC_2H_5	0.5 N		0.25 N	
Vol. taken for each titration	10 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	25.05	0 min.	25.06
	∞	25.22	∞	25.53
		25.24		25.54
Per cent. ester at equil.		1.44		1.88

Conc. KOC_2H_5	0.125 N		0.0625 N	
Vol. taken for each titration	20 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	12.48	0 min.	6.28
	10 "	12.58	10 "	6.34
	60 "	12.70	∞	6.62
	∞	12.86		6.64
		12.84		6.65
Per cent. ester at equil.		1.48		1.44

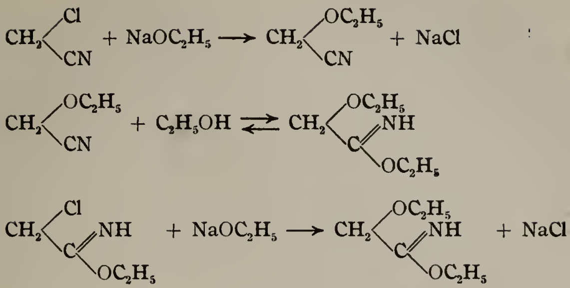
Chloroacetonitrile

Chloroacetonitrile was made as described by Bisschopinck.[1] It was redistilled several times over phosphorus pentoxide and then alone.

The action of sodium ethylate on the chloroacetonitrile does not consist in the simple addition of alcohol with formation of the imido ester. The sodium ethylate, besides acting as catalyst, replaces the chlorine by an ethoxy group with formation of sodium chloride, which after sufficient time precipitates. The following reactions probably take place:



[1] Ber. d. chem. Ges., **6**, 732. Bauer: Ann. Chem. (Liebig), **229**, 167. Scholl and Steinkopf: Ber. d chem. Ges., **29**, 2417; **41**, 2540. Acree and Loy: This Journal, **45**, 227.



The data obtained show that the equilibrium point is widely different from that of the other aliphatic nitriles studied. The alkalinity of a mixture of sodium ethylate and chloroacetonitrile first increases with time and then begins to decrease.

Table XX.—0.25 N Chloroacetonitrile and Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.25 N		0.0625 N	
Vol. taken for each titration	10 cc.		10 cc.[1]	
t	cc. 0.2 N HCl	t	cc. 0.2014 N HNO_3	cc. 0.1 N $AgNO_3$
0 min.	12.50	0 min.	3.10	0.00
9 "	23.06	5 "	14.66	0.50
20 "	23.36	18 "	14.64	0.39
29 "	23.68	38 "	14.60	0.65
47 "	23.46	67 "	14.35	0.82
77 "	23.25	156 "	14.25	0.90
19 hrs.	18.25	178 "	14.08	1.10
24 "	17.48	27 hrs.	12.61	1.34[2]
48 "	13.49			
Per cent. ester[3] at equil.	81.0		94.0	

[1] The solutions were first titrated with nitric acid to neutrality, then the chlorine determined with silver nitrate and potassium chromate.

[2] Sodium chloride had precipitated.

[3] The equilibrium points are not accurate, owing to the complications of the reactions, but the data show that the equilibrium is markedly different from that of the other aliphatic nitriles studied.

Propionitrile and Propimido Ethyl Ester

The propionitrile was obtained from Kahlbaum, and was purified by distilling twice over a little phosphorus pentoxide, and then alone.

Propimido ethyl ester hydrochloride was prepared by treating a mixture of nitrile and alcohol cooled with ice with dry hydrochloric acid gas as described by Pinner.[1] This was allowed to stand overnight in ice, and then the oily mass of crystals filtered and washed with dry ether (Sample *A*). The filtrate was allowed to stand a day longer when more crystals were obtained (Sample *B*).

Analysis of Sample *A*:

0.1587 gram required 11.86 cc. 0.1 N $AgNO_3$. Found chlorine, 26.50 per cent.; theoretical, 25.78 per cent.

Analysis of Sample *B*:

0.1491 gram required 11.34 cc. 0.1 N $AgNO_3$. Found chlorine, 26.96 per cent.

Table XXI.—0.25 N Propionitrile and Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.5 N		0.125 N	
Vol. taken for each titration	10 cc.		20 cc.	
	t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
	0 min.	25.00	0 min.	12.50
	3 "	25.05		
	10 "	25.09	∞	12.97, 12.92
	39 "	25.21		
	∞	25.22, 25.22, 25.21		
Per cent. ester at equil.	1.76		1.76	

[1] *Loc. cit.*, page 28.

Table XXII.—0.25 N Propimido Ethyl Ester and Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.5 N		0.125 N
Vol. taken for each titration	10 cc.		20 cc.
t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
0 min.	37.50	0 min.	37.50
5 "	33.37	5 "	35.13
20 "	27.96	25 "	29.29
31 "	26.73		
46 "	25.86	∞	14.36
62 "	25.75		14.32
	25.56 [1]		
∞	25.58		
	25.56		

Butyronitrile

Butyronitrile was obtained from Kahlbaum and was purified by distillation, first over phosphorus pentoxide and then alone.

Table XXIII.—0.25 N Butyronitrile and Varying Concentrations of Sodium Ethylate

Conc. $NaOC_2H_5$	0.5 N		0.25 N		0.125 N
Vol. taken for each titration	10 cc.		20 cc.		20 cc.
t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
0 min.	25.00	0 min.	25.03	0 min.	12.46
5 "	25.01	∞	25.26	∞	12.69
25 "	25.04		25.28		12.71
52 "	25.07				
	25.10				
∞	25.13				
	25.12				
	25.11				
Per cent. ester at equil.	0.89		0.96		0.96

[1] The equilibrium point could not be determined accurately to compare with that obtained by starting with the nitrile, owing to the decomposition of the imido ester hydrochloride into ammonium chloride in the time required to prepare the solutions, and also to a contamination of the imido ester hydrochloride with ammonium chloride.

The imido ester from this nitrile was not prepared, as, from the description of it by Pinner,[1] it was deemed too unstable to work with.

Diisoamylcyanoamide and Ethyl Diisoamylisourea

Diisoamylcyanoamide and Sodium Ethylate.—The diisoamylcyanoamide was prepared as described by McKee.[2] It was purified by redistillation *in vacuo*. The ethyl diisoamylisourea was prepared from the cyanoamide and sodium ethylate according to McKee's[3] directions, and was purified by fractionation *in vacuo*. The reaction between the cyanoamide and alcohol in the presence of sodium ethylate goes very slowly at 25°. Attempts to follow the reaction by the titration of the isourea formed give only approximate figures as the cyanoamide itself titrates slightly with hydrochloric acid, and makes the end point very uncertain.

Table XXIV.—0.25 N Diisoamylcyanoamide and 0.25 N Sodium Ethylate

At 25°[4]		At 100°[5]	
t	cc. 0.2 N HCl	*t*	cc. 0.2 N HCl
0 min.	12.49	0 hrs.	12.48
3 "	12.56	1 "	23.10
30 "	12.66	2 "	23.30
75 "	12.80	4 "	23.80
17 hrs.	14.02	7 "	24.30
21 "	14.38	11 "	24.40
25 "	14.62	95.36 per cent. isourea formed.	
120 "	19.34		
10 days	23.10		

Ten cc. of the above mixture was allowed to stand at 25° for *ten* days. It required 23.1 cc. 0.2 N hydrochloric acid

[1] *Loc. cit.*, page 30.

[2] This Journal, **36**, 208.

[3] *Ibid.*, **42**, 1.

[4] Ten cc. taken for each titration.

[5] Fifty cc. portions of the two solutions were mixed and 10 cc. portions placed in small tubes, sealed, and heated for the required time in a boiling water bath, and then titrated. Probably equilibrium had not been attained in these experiments.

for neutralization. Therefore, the reaction goes as far in one hour at 100° as in ten days at 25°.

Ethyl Diisoamylisourea and Sodium Ethylate.—The purity of the isourea was tested as follows: 0.5785 gram was poured into water and titrated with 0.2 N hydrochloric acid, using methyl orange as indicator. Required, 12.73 cc.; theoretical, 12.67 cc.

Table XXV.—0.25 N Diisoamylisourea and 0.25 N Sodium Ethylate[1]

t	cc. 0.2 N HCl
0 hours	25.31
0.5 "	25.25
1 "	25.00
3 "	24.94
5 "	24.96
9 "	24.99

2.08 per cent. cyanoamide formed

In this case (also chloracetonitrile) we have a reaction which goes almost to completion to form the isourea (corresponding to the imido ester); while in the case of the acetonitrile, propionitrile and butyronitrile, the reaction proceeds almost entirely in the other direction, to form the nitrile from the imido ester. The other nitriles studied show intermediate values of the equilibrium point.

[1] Equal amounts of the two solutions were mixed and 10 cc. portions placed in small tubes, sealed, and heated for different time periods at 100°, and then titrated.

General Summary

Table XXVI.—Nitriles, or Imido Esters, and Sodium Ethylate in Absolute Ethyl Alcohol at 25°

Nitrile	Conc. of nitrile or imido ester at beginning	Conc. of sodium ethylate	Per cent. imido ester at equilibrium from nitrile side	Per cent. imido ester at equilibrium from imido ester side
Benzonitrile	0.500 N	0.500 N	7.60	....
"	0.375 N	0.500 N	8.37	....
"	0.250 N	0.75 N	9.28	8.88
"	0.250 N	0.25 N	9.12	9.60
"	0.250 N	0.125 N	9.52	9.52
"	0.125 N	0.500 N	11.12	....
"	0.0625 N	0.500 N	14.08	....
	0.03125 N	0.500 N	14.10	....
p-Tolunitrile	0.250 N	0.250 N	6.80	6.08
"	0.250 N	0.250 N	6.71	....
m-Nitrobenzonitrile	0.0625 N	0.500 N	78.1	78.2
"	0.0625 N	0.250 N	77.7	76.8
p-Nitrobenzonitrile	0.05 N	0.0313 N	61.6	....
"	0.05 N	0.08346 N (KOC_2H_5)	61.6	....
m-Bromobenzonitrile	0.125 N	0.500 N	37.9	37.3
"	0.125 N	0.125 N	38.5	....
p-Bromobenzonitrile	0.15 N	0.00781 N	27.17	....
"	0.15 N	0.0039 N	27.17	....

p-Chlorobenzonitrile	0.10 N	0.0625 N	25.85	....
Acetonitrile	0.500 N	0.500 N	1.44	....
"	0.250 N	0.500 N	1.68	....
"	0.250 N	0.500 N (KOC_2H_5)	1.44	....
"	0.250 N	0.250 N	1.80	....
"	0.250 N	0.250 N (KOC_2H_5)	1.88	....
"	0.250 N	0.125 N	1.64	....
"	0.250 N	0.125 N (KOC_2H_5)	1.48	....
"	0.250 N	0.0625 N	1.80	....
"	0.250 N	0.0625 N (KOC_2H_5)	1.44	....
"	0.125 N	0.250 N	2.48	....
"	0.0625 N	0.250 N	2.56	....
Chloroacetonitrile	0.25 N	0.25 N	81.00	(?)....
"	0.25 N	0.0625 N	94.00	(?)....
Propionitrile	0.250 N	0.500 N	1.76	....
"	0.250 N	0.125 N	1.76	....
Butyronitrile	0.250 N	0.500 N	0.89	....
"	0.250 N	0.250 N	0.96	....
"	0.250 N	0.125 N	0.96	....
Diisoamylcyanoamide at 100°	0.250 N	0.250 N	95.36	2.08

It is evident then that the equilibrium point varies very widely when we start with different nitriles in different concentrations, the amount of imido ester left at equilibrium being represented by 1, 1.75, 6.8, 9.2, 14.1, 25.85, 27.17, 38.5, 61.6, 78, and 95 per cent. for different compounds.

CONCLUSIONS

(1) The experimental work shows that nitriles add ethyl alcohol reversibly in the presence of sodium, potassium and lithium ethylates. The per cent. of imido ester present when equilibrium is attained is practically the same whether we start with the nitrile or the imido ester. The equilibrium point varies very widely with the different nitriles.

(2) A few experiments given in this article and other unpublished work show that the reaction velocity can be expressed as a function of the concentration of *both* the ethylate ions and the nonionized ethylate salts.

JOHNS HOPKINS UNIVERSITY
December 1, 1912

REPORT

A CHEMICALLY ACTIVE MODIFICATION OF NITROGEN

It has been frequently observed that vacuum tubes, subjected to an electric discharge, show a luminosity of the contained gas after the discharge is over. If the tube contains carefully purified nitrogen there is no appreciable afterglow when the ordinary discharge is used, but with the jar discharge there is a distinct yellow glow after the discharge is stopped, the glow gradually fading and disappearing completely after about one minute.

This glowing nitrogen has some very remarkable properties which have recently been made the subject of an extended study by Strutt and Fowler.[1]

The glow gives a characteristic band spectrum, otherwise unknown, the most conspicuous bands being green, yellow and red, of approximately the same intensity. The spectrum is similar to the ordinary nitrogen spectrum obtained by using the uncondensed discharge, but is not identical with it. Many

[1] Strutt: P. Roy. Soc., [A] **85**, 219. Fowler and Strutt: *Ibid.*, **85**, 377. Strutt: *Ibid.*, **86**, 56. Strutt and Fowler: *Ibid.*, **86**, 105. Strutt: *Ibid.*, **86**, 262. Strutt: *Ibid.*, **87**, 179.

of the nitrogen bands are wanting and there are certain bands not present in the nitrogen spectrum. The experiments carried out seem to point to the view that, under the influence of the discharge, ordinary nitrogen is converted into an allotropic modification, probably monatomic, which reverts rapidly to ordinary nitrogen. The glow is regarded as a phenomenon accompanying this reversion to the ordinary form.

Chemical Properties

Glowing nitrogen pôssesses remarkable chemical properties. When it is drawn through a tube containing a pellet of yellow phosphorus a violent reaction occurs, the glow is destroyed, red phosphorus is formed and nitrogen is absorbed. In contact with iodine vapor at the ordinary temperature, a "magnificent light blue flame" is produced. A reaction also takes place when sulphur and aersnic are gently heated in the glowing gas. Selenium, carbon, antimony and hydrogen are without effect. When oxygen is admitted the glow is quickly destroyed, but no combination takes place. The oxygen appears to destroy the glow catalytically. If there is any trace of oxygen in the nitrogen that is led into the discharge tube, no afterglow is produced. When metallic sodium is heated a little above its melting point in contact with the glowing nitrogen, the complete sodium spectrum is developed and nitrogen is absorbed. When the metal is heated to 250° the yellow line *D* becomes almost invisible and the green line *E* shows up strongly. There is also a reaction with mercury vapor, forming an explosive compound and developing the mercury spectrum.

Of particular interest is the reaction with nitric oxide. When this gas is mixed with glowing nitrogen, a brilliant flame is produced and nitrogen peroxide is formed. The reaction is represented thus: $2NO + N \longrightarrow NO_2 + N_2$. Advantage is taken of this reaction to determine the percentage of active nitrogen formed in the discharge tube. An excess of nitric oxide is mixed with the glowing nitrogen immediately after it leaves the discharge tube and the mixture of gases led through a U-tube cooled by liquid air. At the low temperature nitrogen peroxide combines with more nitric oxide to form the trioxide, which condenses to a blue liquid. From the weight of nitrogen trioxide formed the percentage of active nitrogen is calculated. The maximum amount obtained is 2.46 per cent.

Active nitrogen reacts with acetylene, forming cyanogen, and with a large number of organic compounds containing

halogens, forming in every case cyanogen and liberating the halogen.

Certain substances, notably copper oxide and manganese dioxide, destroy the glow very quickly, without themselves undergoing any change, apparently. The reaction is regarded as catalytic.

Effect of Temperature

When a stream of glowing nitrogen is drawn slowly through a tube cooled by liquid air, the glow is greatly increased in brilliancy and dies out completely before the coldest part of the tube is reached. When the gas is drawn through a tube moderately heated in one part, the glow is locally extinguished, but reappears farther along the tube. From these experiments it appears that the rate of transformation of active into ordinary nitrogen, of which the intensity of the glow is regarded as an index, is accelerated by lowering and retarded by raising the temperature. The experiments are, however, not conclusive, because of changes in density, which, independently of temperature changes, affect the rate of transformation. Density changes may be avoided by employing sealed bulbs containing glowing nitrogen. Under these conditions the glow is much brighter and of shorter duration when the bulb is immersed in liquid air than when maintained at room temperature. When a similar bulb is immersed in boiling water the life of the glow is again somewhat shortened, though less than before, and the intensity of the glow is very much less.

Still the phenomena are somewhat complicated. There are here two factors affecting the rate of transformation. One is the direct temperature effect, the other is the catalytic effect of the walls of the vessel, also variable with the temperature. Conclusive experimental evidence is adduced to show that the walls of the containing vessel exert a catalytic action and it seems very probable that this effect increases with rise in temperature, as with copper oxide. Strutt concludes that, were it not for the increased catalytic action of the glass walls at the higher temperature, the duration of the glow would be increased in proportion to the diminution of the intensity and points out that we have here a chemical reaction, viz., the transformation of active into ordinary nitrogen, which is entirely unique in that the velocity is accelerated by lowering and retarded by raising the temperature.

Effect of Density

When active nitrogen is compressed, the glow increases in brilliancy and when the gas is restored to its original volume

the glow is less intense than it would have been after the same time interval without compression. Increase of concentration, therefore, not only increases the luminosity, as might have been predicted since the luminosity depends on the amount of transformation per unit volume, but also increases the total change. From this Strutt concludes that the reaction must be other than monomolecular. The evidence here, however, as described, does not seem entirely conclusive, as Strutt appears to have neglected to take into account the increased catalytic action of the walls of the vessel at the higher concentration. It seems obvious that, admitting a catalytic action of the glass, the effect of this action would be greater the more concentrated the gas. The conclusion, however, is not necessarily vitiated by this apparent omission.

Ionization Attendant on Active Nitrogen

When two electrodes, with a difference of potential of two volts, are introduced into glowing nitrogen the amount of current that passes is great enough to be detected by means of an ordinary galvanometer. The ionization is approximately equal to that of a salted Bunsen flame. Rough quantitative measurements show that, assuming that each ionized molecule of active nitrogen furnishes one positive and one negative ion, one out of every fifteen hundred molecules is ionized. This small degree of ionization, as compared with the total quantity of active nitrogen present, leads to the conclusion that the chemical properties of glowing nitrogen are due to the presence of a definite chemical substance and not to some unexplained survival of the conditions of the discharge, and that the formation of ions is a secondary phenomenon associated with active nitrogen or produced by its reversion to the ordinary form. This view is in harmony with the fact that, when the glowing gas is subjected to the influence of an electric field strong enough to remove any ions that may have resulted directly from the discharge, the intensity of the glow is not diminished.

Strutt is led to the same conclusion in regard to the presence in glowing nitrogen of a definite chemical substance by a study of the energy changes accompanying the disappearance of the glow. He finds that when the glow is destroyed by contact with copper oxide, the amount of heat liberated is comparable with that evolved in other gaseous reactions.

Spectra Produced by Active Nitrogen

As already pointed out, glowing or "active" nitrogen reacts readily with a large number of elementary and com-

pound substances, in some instances at room temperature and in others at moderately elevated temperatures, striking luminosity effects being produced in many cases. In general, the spectra developed are not very different from those obtained by other methods, but in some cases additional lines are shown, especially in the more refrangible parts of the spectrum. Thus the spectra of iodine, tin chloride, mercuric iodide, cuprous chloride and cyanogen are more completely developed than by other means. Sulphur gives a series of bands which are quite distinct from those given by sulphur in a vacuum tube.

From a study of the reactions of active nitrogen, Strutt is led to some interesting speculations concerning reactions in general. Apparently no direct observations of volume changes during transformation have been made and the determination of the ratio of specific heats of active nitrogen probably presents insuperable difficulties. It therefore cannot be said positively that this substance is monatomic, but its reactions in general are best explained on the assumption of the monatomic molecule. Making this assumption, the transformation of active into ordinary nitrogen appears to be unique in two particulars: 1. It is the only reaction studied in which both reacting substances are monatomic, that is, two monatomic molecules react, nonreversibly. to form a diatomic molecule, and 2. It is the only known reaction the velocity of which has a negative temperature coefficient. It is suggested that this is not accidental but that the two are causally related.

The kinetic theory requires that when heat is added to a gas consisting of polyatomic molecules the added energy goes partly to increase the translational velocity of the molecules and partly to increase the internal motion of the molecules, and that in monatomic gases the entire heat energy added appears in increased translational velocity. It is usually assumed that raising the temperature increases the velocity of reaction by increasing the frequency and violence of collisions. Now assuming active nitrogen to be monatomic, its transformation to ordinary nitrogen is a reaction which we might expect to have a greater temperature coefficient of velocity than is usually the case. But, on the contrary, we find a negative effect. The conclusion that increase of translational velocity, in itself, is a hindrance to reaction is obvious. "If we permit ourselves the analogy of India rubber balls coated with some adhesive substance, the more violent the collision, the less likely it is that the balls will permanently adhere."

It is suggested that for reactions in general in which polyatomic molecules are involved, the increase in translational velocity due to rise in temperature exerts also a positive hindrance, but the simultaneous increase in internal energy more than balances the unfavorable influence of greater translational velocity and, upon the whole, a rapid increase in the rate of combination takes place. B. F. LOVELACE

REVIEWS

DER ENERGETISCHE IMPERATIV. Von WILHELM OSTWALD. Erste Reihe. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. s. 544. Preis: brosch., M. 9.60; geb., M. 10.60.

Under this strange title the author has brought together some fifty short papers covering an extraordinary range of subjects—the peace movement, the reform of the calendar, Sir William Ramsay, the proposed Hamburg University, the philosophy of nature, Esperanto, *auch alle Dinge überhaupt.* The volume exemplifies more than any previous one the amazing abundance and the highly scattering character of Ostwald's present literary production. But in the author's eye this miscellany is a unity, because most of its parts exhibit different aspects of a single idea. The book sets forth the ethics—theoretical and applied—of a physical chemist—an ethics (ostensibly) deduced entirely from the second law of thermodynamics. The *Dissipationsgesetz* is the "universal source of all values" (59); not merely the chief, but the only, end of man, is to delay the increase of the entropy (in Clausius' sense) of the universe. The "energetical imperative" therefore runs: "Thou shalt not squander energy, but utilize it!" The chief practical inferences here drawn from this principle appear to be that one ought to join the *Monistenbund* (13) and also the movement known as *Die Brücke*, for introducing economic methods into intellectual work, primarily by standardizing the *formats* of books and paper (15); that we need an artificial universal language; that wars and standing armies are bad things; and that the fatigue-factor in education should be taken account of by teachers.

For the knowledge of these practical truths (except the first, mankind luckily did not have to wait for the discovery of energetics. It is true that, down to the end of the 18th century, people in general had no clear and vivid sense of the quantitative limitation of the world's usable resources, and consequently no *generalized* apprehension of the problem of conservation. To a sharp practical realization of the fact

of limitation men were first brought by economics (Malthus); next by the Darwinian biology. Of this fact the principle of Clausius undoubtedly gives the final and most striking generalization; and it therefore lends to that important moral discovery of the 19th century—the duty of systematic conservation—a certain additional impressiveness. This Ostwald does well to bring out. But the applications which seem to interest him most are in large part either the most trivial or the most debatable phases of energy-conservation; he makes no attempt to draw out methodically and evaluate judiciously the many possible applications of his "imperative;" and of many important ones he shows little appreciation. As a systematic ethical theory his reasonings scarcely merit discussion. It is obvious that the rational ends of human choice are not *determined* by the law of the degradation of energy. That law merely formulates one of the important conditions of their realization. Energy is worth conserving only because there are concrete human values to which its utilization is contributory. And the conversion of free energy into mechanical work is not good in itself, but only if the work satisfies some desire, or leaves some one free for qualitatively more valuable modes of conscious life.

Chemists will perhaps be especially interested in the pleasantly written sketches of the characters and work of eminent men of science—Pierre Curie, van't Hoff, Abbé, Ramsay—with which the volume concludes; and in the book as a whole as a self-revelation of the ardent, generous and "temperamental" personality of a great chemist—who cannot unqualifiedly be called a great moral philosopher. A. O. LOVEJOY

PHOTOCHEMISCHE VERSUCHSTECHNIK. Von DR. PHIL. ET MAG. CHEM. JOHANNES PLOTNIKOW, Privatdozent der Chemie an der Kaiserlichen Universität zu Moskau. Mit 189 Figuren, 50 Tabellen und 3 Tafeln. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. pp. xv + 371. Price, M. 11.00.

This is a very useful reference book for those engaged upon photochemical investigations. Part I deals with the lamps of various types which are used in the study of the action of light upon chemical compounds. The mercury arc in its various forms is very fully described, including the recently perfected quartz lamps which were first brought out by Heraeus of Hanau. These lamps are extremely useful in all photochemical work, on account of their powerful ultraviolet radiation. They are now manufactured (in a greatly improved form) in this country by the Cooper-Hewitt Co., of Hoboken, N. J., and so far as the experience of the reviewer goes, are far superior

to the German lamps, both in point of durability and intensity. Various other sources of light are next dealt with, such as metallic and carbon arcs, condenser sparks, colored flames, Nernst lamps and X-ray tubes, with considerable data relating to ray filters.

In Part II the author devotes considerable space to light thermostats for investigating photochemical reactions at constant temperature, closing with a brief treatment of methods of making organic preparations which, on account of the sensitiveness to light of the products formed, have to be carried out in total darkness, or in retorts and condensers of deep red glass.

Part III deals with optical measuring instruments, photometry, radiation laws, sensitiveness of the eye, absorption and refraction measurements, and rotation of the plane of polarization.

Lecture experiments are taken up in Part IV, dealing with the following subjects: Laws of photochemical reactions, accelerating action of light, photochemical equilibrium, decomposition of organic compounds by ultraviolet light, and selective absorption; then follows a chapter on fluorescence, phosphorescence and triboluminescence, and a chapter on photoelectric phenomena.

The author is not always particular about his references as, for example, on page 233 he describes Wood's experiments on the fluorescence of iodine and bromine without making any reference at all, and the ultraviolet ray filter of nitrosodimethylaniline, in combination with blue glass or copper sulphate, described by Wood over ten years ago, which he attributes to H. Lehmann. Lehmann's only contribution was the substitution of Zeiss's modern blue uviol glass for the cobalt glass used in the earlier experiment. His references are given at the end of each chapter, and, though very numerous, are nearly useless, as the subject of the paper is never given, and there is no way of connecting any given matter in the text with its reference. The last quarter of the book is made up of very useful tables of the temperature coefficients of photochemical reactions, spectra of the elements, and the values of λ, $1/\lambda$ and $N = c/\lambda \, . \, 10^{12}$ for values of λ from 2000 to 8000 Ångström units, and the functions l^{-x} and $\tan^2 \alpha$.

As the title indicates, the book deals largely with methods of investigation and manipulation, and as such can be recommended as a reference book. R. W. W.

OXIDATIONS AND REDUCTIONS IN THE ANIMAL BODY. By H. D. DAKIN, D.Sc., F.I.C., The Herter Laboratory, New York. Monographs on Biochemistry, Edited by R. H. A. PLIMMER, D.Sc., and F. G. HOPKINS, D.Sc., F.R.S. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. viii + 135. Price, $1.40.

This monograph is an orderly arrangement of a large amount of important but somewhat disconnected material concerning animal metabolism, supplemented, where a logical demand occurs, by results of original investigation. From a long and intimate acquaintance with the subjects discussed, the author has acquired certain definite ideas of animal metabolism and he proceeds to show that these ideas follow of necessity from the facts of the case. Ample opportunity, however, is given to those who are disposed to differ from him and the best arguments for refuting his theory are always furnished. On page 64 we read: "*The writer is of the opinion that the path of phenylalanine and tyrosine katabolism does not lie by way of homogentisic acid.*" But the writer frankly adds: "*The opposite view is, however, very commonly held,*" and proceeds to show how a benzene derivative with a hydroxyl group substituting position *three* may give rise in the organism to a compound in which the substituting hydroxyl group occupies position *four*. This is the key to the method of discussion employed throughout, but the writer's view is always presented in a manner sufficiently forceful to leave no room for misunderstanding.

At the outset, the importance of a knowledge of intermediate metabolism is explained, various sources of such information are critically discussed, and possible sources of error pointed out. There follows a consideration of ingenious theories of oxygen activation and, in the treatment of Traube's peroxide theory the reader is unconsciously prepared for the complicated matters which constitute the body of the book. Among the more important of these may be noted β-oxidation, the acetone substances, oxidation of side chains, alkaptonuria, tryptophane and the quinoline ring, lactic acid in its relation to carbohydrate metabolism, and the oxidation of purine derivatives.

But of especial interest is a chapter on the oxidation of α-amino acids in which the ground is taken that these substances give rise in the organism primarily to α-ketonic acids and not, as might have been supposed, to α-hydroxy acids. A number of matters are brought into harmony with this assumption. The ketonic acid is proposed as a connecting link between amino acids and carbohydrates and the argument culminates in a discussion of the experiment of Neubauer who

found that *d*-phenylacetic acid is converted by the dog's organism into *l*-mandelic acid—a result which seems to find its only explanation in ketonic acid formation.

The monograph is all that could be reasonably demanded of a text-book and more. It is fully up to the high standard of its companions in the Plimmer-Hopkins series.

WALTER JONES

DIE CHEMISCHE INDUSTRIE IN DEN VEREINIGTEN STAATEN UND DIE DEUTSCHEN HANDELSBEZIEHUNGEN. Auf Grund von amtlichem Material bearbeitet von DR. HERMANN GROSSMANN, Privatdozent an der Universität Berlin. Leipzig: Verlag von Veit & Co. 1912. pp. iv + 85. Price, M. 3.50.

This is a study of the chemical industries of the United States set forth for the benefit of the students of this subject in Germany and for that of the German manufacturer and merchandizer in the products of this industry. The author states that it is "auf Grund von amtlichem Material" and singularly, for a study presented by a privatdozent of the University of Berlin, very meager references are given to the sources from which the very considerable number of statistical tables which are presented have been compiled. The internal evidence shows that publications of the Bureaus of the Census and of Statistics and the Geological Survey have been made use of, but apparently in many instances secondary sources have been resorted to, though the original official publications are most freely at command and readily accessible. The chief reliance seems to have been placed on the Glossary of Schedule A published by the Tariff Board, which is a résumé of much of the official material contained in the above mentioned documents, but the tabular presentations made by the author do not usually coördinate with those of the last mentioned official document, or any of the others.

The subject is treated under the headings of "Die wirtschaftliche Entwicklungsgeschichte der nord-amerikanischen chemischen Industrie. Einfuhr und Ausfuhr von Chemikalien in der Gegenwart;" "Aus der wirtschaftlichen Entwicklungsgeschichte einzelner Zweige der amerikanischen chemischen Industrie;" "Der Handelsverkehr in Chemikalien zwischen Deutschland und den Vereinigten Staaten und die deutsche Handelsstatistik;" "Der neue Zolltarifentwurf für Chemikalien vom Jahre 1912;" "Anhang. Patente und chemische Industrie in den Vereinigten Staaten, von B. Herstein."

It is evident that the narrow view of the chemical industries which prevails in some quarters has controlled the mind of the author and that he has overlooked that broader view

which dominates in academic circles and which was set forth in the *Transactions of the American Institute of Chemical Engineers*.[1] He has, in consequence, overlooked that broader treatment of the patent relations which followed as a consequence of this more extended consideration of the realm of chemical technology.

The brochure is of interest as illustrating to American students the close relations existing in German universities between the investigator, the community, the state and the manufacturer, and as suggesting that there still exists in this country an unfulfilled duty of usefulness awaiting the university officer.

CHARLES E. MUNROE

ELEMENTARY APPLIED CHEMISTRY. By LEWIS B. ALLYN, Department of Chemistry, State Normal School, Westfield, Mass. Boston, New York, Chicago, London: Ginn & Co. pp. xi + 127.

This little book gives an extreme example of a tendency which is observed to too great an extent to-day in educational methods in this country. The revulsion of feeling from the former classical methods of education has produced a demand, even a mania, for things of direct practical value. That education is primarily for the development of the mind is a principle which seems to have fallen into disregard.

The reviewer rejoices with others that matters which have a direct bearing on the problems of life are coming to be recognized as a fit basis for intellectual training. The natural sciences develop the mind to fully as great activity and they give a broader view of life than do the ancient languages. But much of the unsystematic "Nature Study" of to-day, as well as chemistry from the vocational and informational standpoint, serves hardly more than to entertain the pupil; it adds little to his intellectual power, and the mere information, without the intellectual power to apply it to new problems, is of little value even in "practical life."

The book under consideration gives many tests, for the most part empirical, upon such materials as textile fabrics, soils, plants, foods, tooth powders, headache powders, wall papers, paints and oils, and urine. It devotes one section to procedures for dyeing raffia with natural and artificial colors, and another to the removal of stains. This book is only a laboratory guide and does not attempt to explain the chemistry of the materials examined. A few of the tests are for substances which could come within the comprehension of elementary students, and likewise a few of the reactions involved are of

[1] Vol. **2**, 84-104 (1909).

a definite and sufficiently simple character to serve as a basis for the elementary study of chemistry. The mass of the material, however, is purely empirical, or its chemistry is far too complicated to be understood by beginners.

It is certain that this kind of laboratory work will arouse the interest and enthusiasm of a class of normal school students. Perhaps the author succeeds, with the impetus of this enthusiasm, in developing the scientific side of the subject in the classroom. These laboratory experiments, however, are not a suitable basis for an intelligent and logical study of the science of chemistry either in the laboratory or the classroom.

Assuming that for the purpose of arousing enthusiasm this sort of laboratory work is warranted, the book has much that is commendable. Considerable skill has been shown in compiling and adapting methods of testing foods and other products for students unpracticed in chemical manipulation; and some apparently original as well as ingenious and effective methods have been introduced. Too many inaccuracies and ambiguities in statements of facts and in directions are noted and these would frequently perplex a painstaking student.

Experts in food analysis often make mistakes, but they at least understand the complexity of their problem and realize when it is unsafe to give too much weight to their conclusions. It is difficult to see how an elementary pupil (not necessarily limiting the beginner to this class) can make of the course in question more than an attractive form of play, but there is some danger that the play may be taken in earnest and that the student may attain so much false confidence that harm may result from mistaken conclusions.

When all is said, there is no royal road to attainment, except that which involves diligent, and at times uninteresting, plodding. Nevertheless, pupils and sometimes even teachers become filled with the pride of accomplishment if they can jump at once to the attack of important problems and delude themselves that they are accomplishing something while others more methodical would still be laboring to prepare themselves in the rudiments.

In conclusion, the reviewer offers the opinion that, although it is most commendable to add interest to the study of chemistry through its applications to practical problems, it is essential to start with simple substances within the comprehension of the student, and that it is a mistake, even in a brief course, to venture deeper into involved practical matters than the student's understanding will warrant. Arthur A. Blanchard

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Volume V. Tannins, Analysis of Leather, Dyes and Colouring Matters, Dyestuffs of Groups 6 to 12, Colouring Matters of Natural Origin, Analysis of Colouring Matters, Colouring Matters in Foods, Inks. By the Editors and the following contributors: W. P. DREAPER, J. F. HEWITT, W. M. GARDNER, ALBERT F. SEEKER, PERCY H. WALKER, E. FEILMANN. Fourth Edition. Entirely Rewritten. Edited by W. A. DAVIS, B.Sc., A.C.G.I., Formerly Lecturer and Assistant in the Chemical Research Laboratory, City and Guilds College, Imperial College of Science and Technology, London, and SAMUEL S. SADTLER, S.B. Philadelphia: P. Blakiston's Son & Co. 1911. pp. ix + 704. Price, $5.00.

The text of the present volume has been prepared by six contributors, each of established reputation in his chosen topic. Developments in the field covered since the issue of the preceding edition have made necessary many additions and changes in the subject matter. These have on the whole been very judiciously effected without radically altering the general arrangement.

The chapters on tannins and their analysis, and on the analysis of leather are furnished by W. P. Dreaper, and include in their new matter the standard American and European "official" methods. The general description of the properties, reactions, classifications, and uses of the dyestuffs occupies 320 pages, or nearly half the reading matter of the volume. The section on nitro, nitroso, azoxy, pyrazolone, azo, and hydroxyketone colors is the work of W. P. Dreaper and E. Feilmann. The synthetic colors belonging to other classes are treated by J. F. Hewitt, while M. W. Gardner describes the colors of natural origin. The chemical examination of coloring materials in substance, on fibers, or in lakes, is treated in 186 pages by Messrs. Dreaper and Feilmann, Green's most recent procedures, supplemented by tables giving the color reactions of the dyed fibers with acids, alkalies and stannous chloride, being given in full. The chapter of 45 pages by A. F. Seeker on coloring matters in foods is an entirely new section of the book which adds materially to its value. The final chapter, by P. H. Walker, deals with the examination of inks, ink marks, typewriter ribbons, and carbon papers.

There is no question that this volume deserves a place in every library where it has proved its worth in the preceding edition.

S. P. MULLIKEN.

Vol. XLIX March, 1913 No. 3

AMERICAN CHEMICAL JOURNAL

SATURATED δ-KETONIC ESTERS AND THEIR DERIVATIVES

By Dorothy A. Hahn and Angie G. Allbee

In 1897 Vorländer[1] found that ethyl malonate combines with benzylidenacetophenone in the presence of sodium alcoholate, and that it is possible to get a saturated ketonic acid by hydrolyzing the product. Last year Kohler[2] showed that the addition product itself can be isolated in solid form if piperidine is used instead of sodium alcoholate as a condensing agent, and also that it is possible to use this addition product for getting unsaturated δ-ketonic acids. We undertook an investigation of the same reaction, but used anisyl styryl ketone with the expectation that this substance would give crystalline products that would be better adapted for a study of the isomerism that appeared in the unsaturated compounds.[3] As it will take a considerable time to complete the work with the unsaturated compounds, we thought it best to publish an account of the results that have been obtained with the saturated ketonic esters and their derivatives.

Malonic esters do not combine nearly so readily with anisyl styryl ketone as they do with phenyl styryl ketone. We first tried the condensation with sodium alcoholates, but found

[1] Ann. Chem. (Liebig), **294**, 332.

[2] This Journal, **46**, 474.

[3] *Ibid.*, p. 476.

that while it was possible to show, by hydrolyzing the product, that some addition had taken place, it was not possible to isolate solid esters either with ethyl or methyl malonate. Better results were obtained with piperidine. After boiling an alcoholic solution containing equimolecular amounts of unsaturated ketone and ethyl malonate for seventy-two hours—the time that sufficed for complete addition to phenyl styryl ketone—we obtained a mixture of solids that, on separation, yielded about 20 per cent. of the possible amount of pure addition product, the remainder of the solid consisting mainly of unchanged ketone. The yield was increased by longer boiling, but the by-products also increased, and too prolonged heating resulted in a mixture that no longer solidified on cooling.

Diethyl (β-Anisoyl-α-phenylethyl)malonate, $CH_3OC_6H_4COCH_2CH(C_6H_5)CH(CO_2C_2H_5)_2$.—The best results were obtained by dissolving gram molecular quantities of the ketone and the ester in 200 cc. of absolute alcohol, adding 10 grams of piperidine, and boiling this solution continuously for six weeks. The product solidified upon cooling. After filtration and washing with alcohol, it was recrystallized from alcohol; this gave 200 grams of pure ester, a yield of about 50 per cent.

Analysis:

I. 0.1423 gram substance gave 0.3606 gram CO_2 and 0.0807 gram H_2O.

II. 0.1407 gram substance gave 0.3565 gram CO_2 and 0.0773 gram H_2O.

	Calculated for $C_{23}H_{26}O_6$	Found I	Found II
C	69.37	69.1	69.1
H	6.50	6.3	6.1

The ester is readily soluble in ether and hot alcohol. It separates from alcohol in coarse needles or plates melting at 78°.

Dimethyl (β-Anisoyl-α-phenylethyl)malonate, $CH_3OC_3H_4COCH_2CH(C_6H_5)CH(CO_2CH_3)_2$.—The unsaturated ketone combines more rapidly with the methyl than with the

ethyl ester of malonic acid, and it was found that the yield of pure product did not increase after boiling for three weeks. The procedure was as follows: Gram molecular quantities of unsaturated ketone and ester were dissolved in 150 cc. of methyl alcohol, 10 grams of piperidine added, and the solution was boiled continuously for three weeks. The solid product was filtered, washed with small quantities of methyl alcohol, and recrystallized from the same solvent. The yield in different experiments varied from 160 to 200 grams, 45 to 50 per cent. of the possible amount.

Analysis:

I. 0.1216 gram substance gave 0.3017 gram CO_2 and 0.0638 gram H_2O.

II. 0.1502 gram substance gave 0.3724 gram CO_2 and 0.0784 gram H_2O.

	Calculated for $C_{21}H_{22}O_6$	Found I	Found II
C	68.1	67.6	67.8
H	5.9	5.8	5.8

The methyl ester is much more easily separated from unchanged ketone than the ethyl ester. It is readily soluble in ether and in hot methyl alcohol, from which it separates in fine needles or plates melting at 104°.

(β-Anisoyl-α-phenylethyl)malonic Acid, $CH_3OC_6H_4COCH_2CH(C_6H_5)CH(CO_2H)_2$.—For the purpose of hydrolysis the ethyl ester was dissolved in alcohol and treated with an excess of concentrated aqueous potassium hydroxide. A crystalline potassium salt separated immediately. This was washed with alcohol, dissolved in a small quantity of water, and reprecipitated by addition of alcohol to the water solution. The salt crystallized from alcohol in fine needles or plates. Analysis:

I. 0.1033 gram substance gave 0.0411 gram K_2SO_4.

II. 0.1077 gram substance gave 0.0428 gram K_2SO_4.

	Calculated for $C_{19}H_{16}O_6K_2.H_2O$	Found I	Found II
K	17.88	17.83	17.88

These results show that the substance is the dipotassium salt of (anisoylphenylethyl)malonic acid. From a concen-

trated aqueous solution of the salt, acids precipitate the corresponding monopotassium salt, and this, in contact with excess of acid, slowly passes into the acid. The acid was purified by crystallization from ether or ethyl acetate.

Analysis:

I. 0.1227 gram substance gave 0.2993 gram CO_2 and 0.0568 gram H_2O.

II. 0.1451 gram substance gave 0.3548 gram CO_2 and 0.0663 gram H_2O.

	Calculated for $C_{19}H_{18}O_6$	Found I	Found II
C	66.6	66.5	66.6
H	5.2	5.1	5.2

(Anisoylphenylethyl)malonic acid crystallizes from water in fine needles containing water of crystallization which it loses below 130°. It is moderately soluble in hot water, but it is not feasible to recrystallize it from water, because, while dissolving, it slowly decomposes with evolution of gas. The acid melts with decomposition at about 165°. If the temperature is kept between 165° and 170° until the evolution of gas ceases, the loss in weight corresponds almost exactly to one molecule of carbon dioxide per molecule of acid.

1.0355 grams substance lost 0.1356 gram.

	Calculated for $C_{19}H_{18}O_6$	Found
CO_2	12.8	13.1

γ-Anisoyl-β-phenylbutyric Acid, $CH_3OC_6H_4COCH_2CH(C_6H_5)CH_2CO_2H$.—The pale yellow liquid, obtained by heating (anisoylphenylethyl)malonate to 165°–170°, was poured, while still hot, into chloroform. From the chloroform solution ligroin precipitated a solid acid which was purified by recrystallization from ethyl acetate.

Analysis:

I. 0.1624 gram substance gave 0.4297 gram CO_2 and 0.0849 gram H_2O.

II. 0.1436 gram substance gave 0.3802 gram CO_2 and 0.0750 gram H_2O.

	Calculated for $C_{18}H_{18}O_4$	Found I	II
C	72.4	72.1	72.2
H	6.0	5.8	5.8

The acid is moderately soluble in hot ethyl acetate and chloroform, sparingly in ether, almost insoluble in ligroin. It separates from ethyl acetate in plates or prisms melting at 152°.

Methyl γ-Anisoyl-β-phenylbutyrate, $CH_3OC_6H_4COCH_2CH(C_6H_5)CH_2CO_2CH_3$.—The ester may be made by saturating a methyl alcoholic solution of the acid with gaseous hydrogen chloride, but it is more easily obtained by starting with the dipotassium salt of (anisoylphenylethyl)-malonic acid. For this purpose the salt is dissolved in water, the solution acidified with hydrochloric acid, and the resulting monopotassium salt immediately filtered, washed with small quantities of water and dried. The dried salt loses carbon dioxide at about 170°. The residue, while still hot, is poured into methyl alcohol and the solution saturated with hydrogen chloride. Potassium chloride is precipitated, and most of the ester separates in solid form when the solution cools. The remainder is readily obtained by concentrating the mother liquors. The ester was purified by recrystallization from alcohol, from which it separated in long plates or prisms melting at 86°.

Analysis:

I. 0.1539 gram substance gave 0.4098 gram CO_2 and 0.0879 gram H_2O.

II. 0.1268 gram substance gave 0.3381 gram CO_2 and 0.0719 gram H_2O.

	Calculated for $C_{19}H_{20}O_4$	Found I	II
C	73.0	72.6	72.7
H	6.4	6.3	6.3

The potassium salt of anisoylphenylbutyric acid was prepared by hydrolyzing the methyl ester. The ester was dissolved in alcohol, the solution treated with excess of strong alcoholic potassium hydroxide, and allowed to stand overnight at ordinary temperature. It was then slowly concen-

trated on a water bath until addition of ether to the cooled solution precipitated a crystalline potassium salt. This was purified by recrystallization from a mixture of alcohol and ether. It is readily soluble in alcohol, sparingly in ether, and crystallizes in minute needles or plates. Its water solution decolorizes potassium permanganate.

Analysis:

0.1082 gram substance gave 0.0270 gram K_2SO_4.

0.1047 gram substance gave 0.0263 gram K_2SO_4.

	Calculated for $C_{18}H_{17}O_4K.H_2O$	Found I	Found II
K	11.01	11.18	11.26

γ-Bromo-γ-anisoyl-β-phenylbutyric Acid,

$CH_3OC_6H_4COCHBrCH(C_6H_5)CH_2CO_2H$.—Two isomeric bromine substitution products were obtained when bromine was added to a solution of anisoylphenylbutyric acid in chloroform. It was necessary to start the reaction by warming the solution, but after that the bromine disappeared as rapidly as added. As soon as one molecule of bromine had been added, part of the solvent was distilled. The residue, on cooling, deposited most of the product in the form of a colorless crystalline solid; the remainder was precipitated by addition of ligroin. The solid was washed with a small quantity of ether, then recrystallized from ethyl acetate. This deposited thin plates melting at 144° with evolution of gas.

The ethereal washings and the mother liquors yielded a second product, which was likewise recrystallized from ethyl acetate. After many recrystallizations it finally showed a constant melting point of 119°. The substance melts without decomposition but begins to give off gas a few degrees above the melting point.

Analysis:

I. 0.1664 gram substance (119°) gave 0.3503 gram CO_2 and 0.0719 gram H_2O.

II. 0.1202 gram substance (144°) gave 0.2535 gram CO_2 and 0.0509 gram H_2O.

	Calculated for $C_{18}H_{17}O_4Br$	Found I	Found II
C	57.3	57.4	57.5
H	4.5	4.7	4.7

The higher melting bromine compound is readily soluble in ethyl acetate and chloroform, moderately in ether, very slightly in carbon tetrachloride and ligroin. The lower melting compound is much more readily soluble in all solvents. Since both substances give the same lactone when treated with sodium carbonate, they must be stereoisomers. The higher melting product is obtained in much the largest quantity.

Methyl γ-Bromo-γ-anisoyl-β-phenylbutyrate, $CH_3OC_6H_4COCHBrCH(C_6H_5)CH_2CO_2CH_3$.—The methyl ester behaves like the acid toward bromine, and like the acid it gives two isomeric bromine substitution products. The reaction was carried out in chloroform. After removing most of the chloroform by distillation, hot methyl alcohol was added to the residue. The solution, on cooling, deposited hard plates that, after one crystallization from methyl alcohol, melted sharply at 122°.

The mother liquors, after concentration, deposited a second product in soft plates or needles that, after crystallization from methyl alcohol, melted at 84°. It was easy to get a complete separation of the two substances, and it was found that about 75 per cent. of the product was composed of the higher melting, the remainder of the lower melting substance. Both substances give the same products when hydrolyzed with potassium hydroxide.

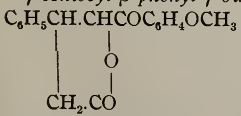
Analysis:

I. 0.1739 gram substance (84°) gave 0.3722 gram CO_2 and 0.0756 gram H_2O.

II. 0.1609 gram substance (122°) gave 0.3448 gram CO_2 and 0.0699 gram H_2O.

	Calculated for $C_{19}H_{19}O_4Br$	Found I	Found II
C	58.3	58.3	58.4
H	4.8	4.8	4.8

γ-Anisoyl-β-phenyl-γ-butyrolactone,



.—The two isomeric bromine substitution products of anisoylphenylbutyric acid behave in

exactly the same way when treated with sodium carbonate. The powdered acids dissolve readily in a cold dilute aqueous solution of the carbonate, the solution remains clear for a short time, then becomes milky, and in the course of half an hour the separation of lactone is complete. Both acids gave the same lactone. This was purified by recrystallization from alcohol or ethyl acetate, from which it separates in large six-sided prisms melting at 109°.

Analysis:

I. 0.1256 gram substance gave 0.3325 gram CO_2 and 0.0588 gram H_2O.

II. 0.1512 gram substance gave 0.4000 gram CO_2 and 0.0711 gram H_2O.

	Calculated for $C_{18}H_{16}O_4$	Found I	Found II
C	72.9	72.2	72.1
H	5.4	5.2	5.2

The lactone is moderately soluble in ether, readily soluble in alcohol, chloroform and ethyl acetate. The same lactone was obtained by hydrolyzing methyl anisoylbromophenylbutyrate, but when prepared in this way it was contaminated by a large quantity of by-products of which one was identified as anisoylphenylbutyric acid.

Diethyl (β-Bromo-β-anisoyl-α-phenylethyl)malonate, $CH_3OC_6H_4COCHBrCH(C_6H_5)CH(CO_2C_2H_5)_2$.—The bromine compound was prepared by adding a small quantity of bromine to a solution of the ethyl ester of (anisoylphenylethyl)malonic acid in chloroform, warming the solution until the reaction started, and then rapidly adding the calculated quantity of bromine. After the reaction had started the bromine disappeared as rapidly as it was added. The solvent was removed by distillation under diminished pressure, and the residue, while still hot, poured into alcohol. The alcoholic solution, on evaporation, deposited an oil that finally solidified when rubbed with a rod after standing for eight weeks. Only one of the two possible stereoisomeric products was isolated in solid form, but both were probably formed because the yield of solid product was only 25 per cent. of the possible amount

and the residual oil gave the same reactions as the solid. The solid was purified by recrystallization from alcohol.

Analysis:

I. 0.1680 gram substance gave 0.3573 gram CO_2 and 0.0802 gram H_2O.

II. 0.1332 gram substance gave 0.2838 gram CO_2 and 0.0636 gram H_2O.

	Calculated for $C_{23}H_{25}O_6Br$	Found I	Found II
C	57.8	58.0	58.1
H	5.2	5.3	5.3

The bromine compound is readily soluble in ether and alcohol. It separates from solution in large six-sided prisms melting at 97°. When treated with potassium hydroxide or sodium ethylate it readily loses hydrobromic acid and forms one or more unsaturated δ-ketonic esters. From the resulting esters, a variety of lactonic acids and both saturated and unsaturated lactones have been obtained; but as the relations between the isomeric substances have not yet been fully cleared up, this part of the investigation will be reserved for a later paper.

Mt. Holyoke College
Laboratory

[Contribution from the Massachusetts Agricultural College]

THE OXIDATION OF ALDEHYDES BY AN AQUEOUS SOLUTION OF BROMINE

By Ernest Anderson

The standard method for converting aldose sugars into the corresponding acids is oxidation by an aqueous solution of bromine.[1] The opinion is prevalent that this method cannot be applied to the ordinary aliphatic and aromatic aldehydes. In order to test this point several aldehydes were treated with an aqueous solution of bromine and the oxidation products isolated. It was found as a result that some of the aldehydes, notably benzaldehyde, acetaldehyde, paraldehyde and formic acid, gave good yields of the corresponding oxidation products, benzoic, acetic and carbonic acids. Other aldehydes gave poor yields of the corresponding acids under the most favorable conditions. This was true of formaldehyde and aldol.

[1] Kiliani: Ber. d. chem. Ges., **17**, 1296.

Still other aldehydes, especially salicylaldehyde and chloral, gave no oxidation products at all. Salicylaldehyde appeared to go directly to tribromophenol while chloral was not attacked by the bromine. On the whole, the method is unsatisfactory, though by careful work it can be used.

The following table gives the amounts obtained, calculated as per cent. of the theoretical yield:

Substance	Acid formed	Yield in per cent.
Acetaldehyde	Acetic acid	71
Benzaldehyde	Benzoic acid	80
Paraldehyde	Acetic acid	86
Formic acid	Carbonic acid	80
Formaldehyde	Formic acid	poor
Aldol	β-Hydroxybutyric acid	poor
Salicylaldehyde	Salicylic acid	none
Chloral hydrate	Trichloroacetic acid	none

EXPERIMENTAL PART

Acetaldehyde.—A mixture of 37 grams of bromine and 25 cc. of water was added to a solution of 10 grams of acetaldehyde in 50 cc. of water. The contents of the vessel were kept at 8° C. during the mixing. The liquid bromine dissolved 15 minutes after mixing. The solution was left in the dark for 36 hours. Then the excess of bromine was removed by a slow stream of air. The hydrobromic acid was precipitated by the careful addition of silver carbonate. The slight excess of silver was precipitated by the addition of sodium carbonate solution. The alkaline filtrate was evaporated to dryness on the water bath. The salt residue was dissolved in a small amount of water, put into a distilling flask with excess of sulphuric acid and the acetic acid distilled over. The distillate, which consisted of water, acetic acid and traces of hydrobromic acid, was mixed with a concentrated solution of silver nitrate containing a slight excess of the salt for the aldehyde used. The silver bromide was filtered off and the silver acetate precipitated by the careful addition of sodium hydroxide to neutrality.[1] A yield of 27 grams of silver acetate

[1] When silver nitrate solution is added to hydrobromic and acetic acids, the silver bromide precipitates from acid solution. If the filtrate is then made just neutral with sodium hydroxide the silver acetate precipitates.

in three crops was obtained. This was purified by crystallization one time from water and gave the following results on analysis:

0.4163 gram salt, dried *in vacuo*, gave on ignition 0.2687 gram silver.

	Calculated for $AgC_2H_3O_2$	Found
Ag	64.67	64.52

The yield obtained is 71 per cent. of the theoretical. There are other products formed, among them one that affects the eyes. Probably the yield would be better if the solutions were more dilute during oxidation.

Paraldehyde.—A mixture of 19 grams of bromine and 50 cc. of water was added to a solution of 5 grams of paraldehyde in 750 cc. of water. The acetic acid was isolated from the oxidation mixture as in the case of acetaldehyde. A yield of 16.3 grams of silver acetate was obtained. This, after one crystallization from water, gave the following results on analysis:

1.3383 gram salt, dried *in vacuo*, gave on ignition 0.8623 gram silver.

	Calculated for $AgC_2H_3O_2$	Found
Ag	64.67	64.42

The yield is 86 per cent. of the theoretical. It could be easily raised to very near the theoretical. Apparently no other products are formed in this oxidation, but this point was not investigated.

Benzaldehyde.—A mixture of 9 grams of bromine and 25 cc. of water was added to 5 grams of benzaldehyde and 25 cc. water. The mixture was left at room temperature for 20 hours, then cooled in ice water and the benzoic acid filtered off. The air-dry substance weighed 3.3 grams and melted at 119° to 121° C. The filtrate was extracted three times with ether. The ether extract was shaken with silver carbonate to remove hydrobromic acid and bromine, and after drying over calcium chloride the ether was distilled off. The residual oil, consisting of benzaldehyde and benzoic acid, weighed 1.7 grams. This was separated by distillation into 0.4 gram

benzaldehyde boiling at 190° C., and 1.2 grams of benzoic acid melting at 118° to 120° C.

The yield is 80 per cent. of the theoretical. The 4.5 grams of benzoic acid, after one crystallization from water, melted at 120° to 121° C. and this melting point remained unchanged when the substance was mixed with chemically pure benzoic acid.

Formic Acid.—A mixture of 20 grams of bromine and 50 cc. of water was added to a solution of 5 grams of formic acid in 500 cc. of water. This solution was connected with a reflux condenser, to the upper end of which were connected four cylinders containing a saturated solution of barium hydrate. A slow stream of air, free of carbon dioxide, was drawn through the apparatus for 15 hours. Finally the formic acid solution was heated in the boiling water bath for 15 minutes to remove all the carbon dioxide. The barium carbonate was filtered off and weighed 26 grams, dried *in vacuo*. This is a yield of 80 per cent.

Formaldehyde.—Thirteen and two-tenths cc. of formalin solution containing 5 grams of formaldehyde were dissolved in 500 cc. water and oxidized with 57 grams of bromine. The carbon dioxide was determined as in the formic acid experiment. The barium carbonate weighed 31 grams. This is a yield of 94.2 per cent.

Repeated attempts were made to oxidize formaldehyde to formic acid with bromine. These always gave a small amount of formic acid which was isolated and analyzed as the lead salt.

One hundred cc. of formalin solution, corresponding to 38 grams of formaldehyde, were dissolved in 900 cc. of water and 195 grams of bromine added. After standing 24 hours the hydrobromic acid was removed by lead carbonate and afterwards by silver carbonate. The lead and silver were precipitated by hydrogen sulphide. The dissolved hydrogen sulphide was removed by heating the solution. The formic acid was isolated by treating the solution with lead carbonate on the boiling water bath, filtering and concentrating *in vacuo*. This gave 35 grams of lead formate which, on crystallization

from water and drying *in vacuo*, gave on analysis the following result:

0.9565 gram substance, on precipitation as the carbonate and ignition, gave 0.7213 gram lead oxide.

	Calculated for $Pb(CHO_2)_2$	Found
Pb	69.7	70.0

Aldol.—A mixture of 70 grams of bromine and 50 cc. water was added to a solution of 36 grams of aldol in 350 cc. of water. The solution became quite warm and considerable oil separated out. After standing 18 hours, the solution was extracted three times with ether to remove the oil. This ether extract gave 15.6 grams thick, dark gum insoluble in water and affecting the eyes badly, which was finally thrown away.

The water solution was treated with silver carbonate to remove hydrobromic acid. The silver was precipitated as silver sulphide and the water distilled off *in vacuo*. The oil was taken up in ether and found to weigh 23 grams. This was treated first with silver carbonate and afterwards with a strong solution of silver nitrate. The solution, which was acid, was made almost neutral by the addition of sodium hydroxide and concentrated *in vacuo*. On the addition of alcohol, 36 grams of crystalline salt, in two crops, were obtained. This was purified by dissolving in 150 cc. boiling water, filtering and adding 300 cc. alcohol. On analysis the pure salt gave the following result:

0.8062 gram substance, dried *in vacuo*, gave on ignition 0.4133 gram silver.

	Calculated for $AgC_4H_7O_3$	Found
Ag	51.19	51.26

The salt showed all the properties of silver β-hydroxybutyrate described by Wurtz.[1]

Salicylaldehyde.—This substance gave a very large amount of tribromophenol and no salicylic acid when it was treated in aqueous solution with bromine.

[1] Jahresbericht, **1870**, 657; **1872**, 449; **1873**, 473.

Chloral Hydrate.—It was found impossible to oxidize this substance in aqueous solution with bromine.

[Contributions from the Sheffield Laboratory of Yale University]

CCV.—RESEARCHES ON PYRIMIDINES

BARBITURYL- AND 2-THIOBARBITURYL-5-ACETIC ACIDS

By Treat B. Johnson and Edward F. Kohmann

[FIFTY-NINTH PAPER]

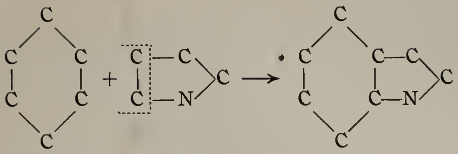
The imidazoles, pyrroles, pyrimidines and pyridines are types of heterocyclic combinations which are of common occurrence among natural substances. These nitrogen cycles functionate in nature's processes not only in their simple forms, but also as condensed nuclei which retain, to a certain degree, the characteristic properties of the simple cycles. For example: Not only do we find the two heterocycles, imidazole and pyrimidine, represented by the amino acid histidine, the Jaborandi alkaloids pilocarpine, isopilocarpine and pilocarpidine,[1] ergothioneine,[2] uracil, thymine and cytosine, but we also find representatives of condensed nuclei of these two rings, the purines (III), widely distributed in both animal and vegetable organisms. The pyrrole compounds are not only found as such in the blood, proteins and chlorophyll of plants, but also in the form of condensed nuclei of this ring with benzene, the indoles (I). This type of nitrogenous compounds is represented by the amino acid tryptophane, and its betaine derivative hypophorine,[3] indigo, skatole and indole. Closely related to the indoles are the corresponding pyridine derivatives, the *pyrindoles* (II), which contain condensed pyridine and pyrrole nuclei. For our present knowledge of this new class of substances we are indebted to Perkins.[4] He has shown that their structure affords an explanation of the unique reactions of the naturally occurring alkaloids, harmine and harmaline.

[1] Pictet and Biddle: Vegetable Alkaloids, p. 171.

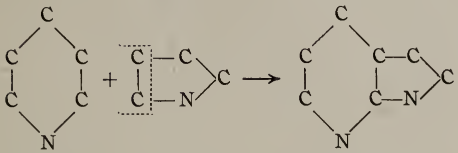
[2] Tanret: J. pharm. chim., **30,** 145. Barger and Ewin: J. Chem. Soc., **1911,** 2336.

[3] Centralb., **1911,** I, 1548.

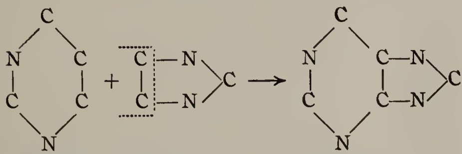
[4] W. H. Perkins and R. Robinson: J. Chem. Soc., **101,** 1775.



(Benzene) (Pyrrole) (Indole) (I)



(Pyridine) (Pyrrole) (Pyrindole) (II)

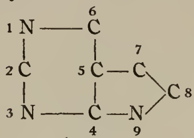


(Pyrimidine) (Imidazole) (Purine) (III)

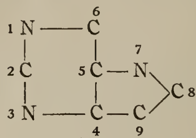
So far as the writer is aware, substances containing condensed pyrimidine and pyrrole nuclei, corresponding to the indoles (I) and pyrindoles (II), represent new types of organic compounds concerning which we have no knowledge. It is therefore of especial interest and desirable to develop methods for their synthesis and investigate their chemical behavior. Such combinations would not only be of physiological interest, but it is also not improbable that such heterocyclic substances may be found to occur in nature. We shall record therefore, in this paper, some results of attempts to obtain representatives of this new class of compounds.

As the nomenclature of compounds containing condensed pyrimidine and pyrrole nuclei presents some difficulties we shall call such substances *pyrimazoles*. Furthermore, since there are three structurally isomeric forms theoretically possible,

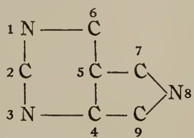
depending upon the position occupied by the pyrrole nitrogen in the condensed nucleus, we shall designate them as 1,3,9- 1,3,7- and 1,3,8-pyrimazoles, as represented by Formulas (IV), (V) and (VI), respectively. The method of numbering the different positions in the ring is analogous to that adopted in the purine series. The numbers before the name *pyrimazole* indicate the positions occupied by the nitrogen atoms in the heterocycle.



(IV)

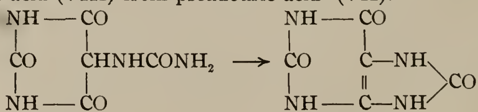


(V)

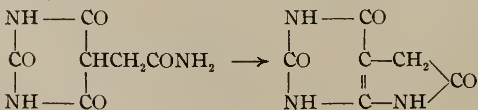


(VI)

Two methods of synthesizing 1,3,9-pyrimazole compounds (IV) which seemed feasible were the following: (1) To prepare a 4- or 6-aminopyrimidine derivative of acetic acid or its ester and then condense to a γ-lactam ring with formation of an oxypyrimazole. (2) To synthesize the amide of barbituryl-5-acetic acid (IX), and then condense this to a pyrimazole (X), with formation of water. A condensation of this nature would be perfectly analogous to that involved in the formation of uric acid (VIII) from pseudouric acid[1] (VII).



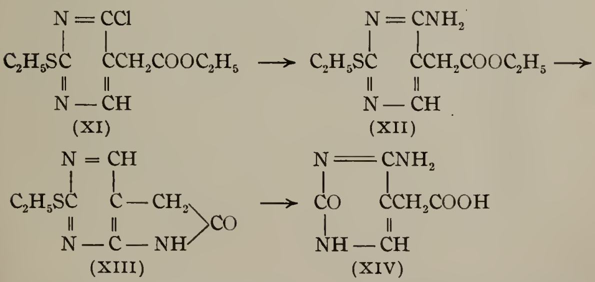
(VII) (VIII)



(IX) (X)

[1] Fischer and Ach: Ber. d. chem. Ges., **28**, 2474. Fischer: *Ibid.*, **30**, 560.

A synthesis of Type 1 has already been applied successfully, and the pyrimazole derivative obtained has been described in a previous paper from this laboratory.[1] It was prepared by heating ethyl 2-ethylmercapto-6-chloropyrimidine-5-acetate (XI) with ammonia. The chlorine atom was displaced by the amino group by this treatment, and the corresponding aminopyrimidine (XII) was formed. This compound then underwent a lactam condensation with evolution of alcohol and formation of the mercaptopyrimazole (XIII). This substance was named 2-ethylmercapto-5,6-(α-pyrolidone)-pyrimidine, but according to our proposed nomenclature it would be called 2-ethylmercapto-8-oxy-1,3,9-pyrimazole. This compound possessed properties of a γ-lactam and consequently underwent hydrolysis when warmed with hydrochloric acid, forming quantitatively cytosine-5-acetic acid (XIV) with evolution of ethyl mercaptan.

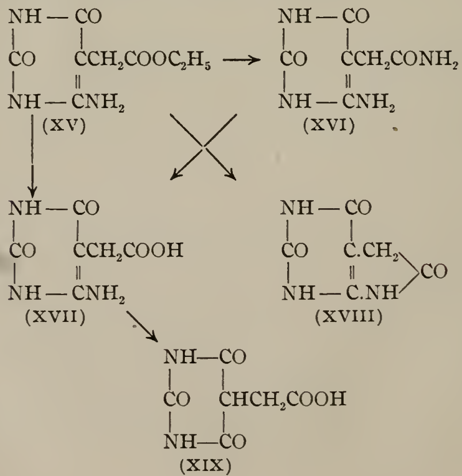


(XI) (XII) (XIII) (XIV)

In order to determine whether pyrimazoles can be obtained by application of this reaction in other cases, we have now investigated the behavior of diethyl α-cyanoethane-α,β-dicarboxylate[2] towards urea. Theoretically this ester would be expected to condense in a manner analogous to that of ethyl cyanoacetate, forming ethyl 2,6-dioxy-4-aminopyrimidine-5-acetate (XV) We now find that this ester does not enter into a smooth reaction with urea, and that the greater proportion of both reagents undergo decomposition when digested

[1] Johnson: J. Am. Chem. Soc., **33**, 758.
[2] Haller and Barthe: Ann. chim. phys., [6] **18**, 283.

together in the presence of sodium ethylate. The results which we obtained showed, however, that a portion of the carboxylate condenses normally, forming the pyrimidine (XV), as expected. This compound was not isolated, but its primary formation was established by the fact that ammonia and barbituryl-5-acetic acid (XIX) were formed when the crude reaction product was digested with hydrochloric acid. Part of the ester undergoes saponification during the digestion, giving the corresponding acid (XVII), part combines with ammonia, forming apparently the amide (XVI), and it also undergoes an inner condensation as expected, forming 2,6,8-trioxy-1,3,9-pyrimazole (XVIII). The yields, however, of these pyrimidines were variable and it was impossible to so control the conditions of the reaction that the pyrimazole could be obtained in large amounts. The pyrimazole was obtained as a light colored powder, which was insoluble in water, and possessed no definite melting point. The amide was not isolated in a pure condition. These various changes are represented by the following structural formulas:



Pseudouric acid (VII) easily undergoes an inner condensation with formation of uric acid[1] when heated with oxalic or hydrochloric acids. Fischer[2] was unable, however, to effect an analogous condensation with 6-thiopseudouric acid. 2-Thiopseudouric and 2-thiouric acids have not been synthesized.[3] These pseudouric acids are closely related in structure to the amides of barbituryl- and 2-thiobarbituryl-5-acetic acids, (XXV) and (XXVI), and consequently it seemed of interest to prepare the latter and determine whether they would undergo a condensation analogous to that of the pseudouric acids, giving the corresponding 1,3,9-pyrimazoles, (XXVIII) and (XXIX). They were obtained by condensation of triethyl ethane-α,α,β-tricarboxylate[4] (XXII) with urea and thiourea, respectively. By the action of this ester on these ureas we expected to obtain the corresponding esters, (XXIII) and (XXIV), and then convert these into their corresponding amides by the action of ammonia. To our surprise, however, the amides were formed in one operation because of the fact that part of the ureas underwent decomposition with formation of ammonia. This then reacted with the esters in alcohol, giving the corresponding amides. Barbituryl-5-acetamide (XXV) was obtained in the form of its sodium salt, which was difficultly soluble in cold water and contained 4 molecules of water of crystallization. Thiourea condensed with the tricarboxylate, giving the corresponding salt of the sulphur pyrimidine, which separated in an anhydrous condition. Both salts dissolved in warm water and on acidifying their respective solutions the amides (XXV) and (XXVI) were obtained.

The ease with which these two esters react with ammonia, forming the amides (XXV) and (XXVI), is remarkable and of especial interest, because it has been our previous experience that esters of pyrimidine acids react with difficulty with ammonia. For example, in order to prepare 2-ethylmercapto-6-oxypyrimidine-5-acetamide (XX) from the corresponding

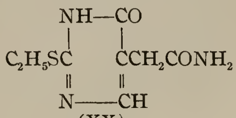
[1] Fischer and Ach: *Loc. cit.*

[2] Fischer and Ach: Ann. Chem. (Liebig), **288**, 157.

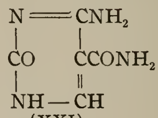
[3] Richter's Lexikon der Kohlenstoffverbindungen.

[4] Wislicenus and Nassauer: Ber. d. chem. Ges., **27**, 797. Bischoff: Ann. Chem. (Liebig), **214**, 38.

ester it was necessary to heat this with ammonia at 140°–150°[1] while, on the other hand, it has been shown that 5-carbethoxycytosine exhibits a remarkable inertness and can not be converted into its corresponding amide (XXI) when heated with ammonia under similar conditions.[2]

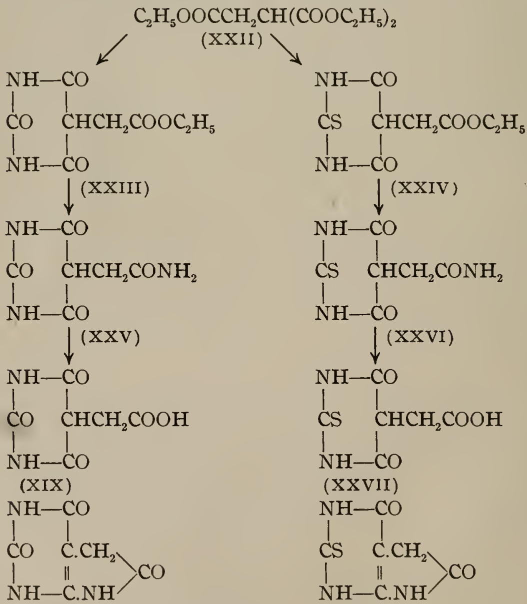


(XX)



(XXI)

Attempts to condense the two amides (XXV) and (XXVI) to the corresponding pyrimazoles were unsuccessful. They were



(XXII) (XXIII) (XXIV) (XXV) (XXVI) (XIX) (XXVII) (XXVIII) (XXIX)

[1] Johnson and Speh: THIS JOURNAL, **38**, 602.

[2] Wheeler and Johns: *Ibid.*, **38**, 594; **40**, 233.

easily decomposed by the action of alkali and hydrochloric acid and underwent hydrolysis, with formation of the corresponding acids, viz., barbituryl-5-acetic (XIX) and 2-thiobarbituryl-5-acetic acids (XXIX), respectively.

EXPERIMENTAL PART

The Condensation of Urea with Triethyl Ethane-α,α,β-tricarboxylate, $C_2H_5OOCCH_2CH(COOC_2H_5)_2$

Barbituryl-5-acetamide,

$$\begin{array}{ll} NH\text{—} & CO \\ | & | \\ CO & CHCH_2CONH_2. \\ | & | \\ NH\text{—} & CO \end{array}$$

— This acid amide was obtained in the form of its sodium salt by digesting urea with triethyl ethane-α,α,β-tricarboxylate in alcohol and in the presence of sodium ethylate. The method of procedure was as follows: Two molecular proportions of sodium (3.4 grams) were dissolved in 75 cc. of absolute alcohol and a molecular proportion of urea (4.4 grams) dissolved in the alkaline solution. Eighteen grams of the tricarboxylate were then added at once, when there was an immediate reaction and a colorless salt separated. The mixture was then heated on a steam bath for about 10–11 hours in order to complete the reaction. The alcohol was finally evaporated and the residue triturated with about 20 cc. of cold water and a little ether, when we obtained the sodium salt of the amide as a colorless crystalline powder. The yield was 6.9 grams. We obtained no precipitate when the aqueous filtrate was acidified with acetic or hydrochloric acids. This sodium salt is insoluble in alcohol, but crystallizes from hot water in slender, colorless prisms arranged in rosettes which have no definite melting or decomposition point. The salt contained four molecules of water of crystallization, which were determined by heating at 120°–125°.

Water determination:

0.4724 gram substance lost 0.1214 gram H_2O.

	Calculated for $C_6H_6O_4N_3Na.4H_2O$	Found
H_2O	25.82	25.7

Nitrogen determination in the anhydrous salt (Kjeldahl):

	Calculated for $C_6H_6O_4N_3Na$	Found
N	20.29	20.31

In order to obtain the free barbiturylacetamide the above sodium salt was dissolved in a small volume of hot water and the solution acidified with hydrochloric acid and cooled. The amide separated in the form of needles and was purified by recrystallization from hot water. It melted from 258°–261° with decomposition. The amide was dried for analysis (Kjeldahl) at 100°.

	Calculated for $C_6H_7O_4N_3$	Found
N	22.7	22.44

```
                             NH—CO
                             |   |
Barbituryl-5-acetic acid,   CO   CHCH2COOH.—This acid was
                             |   |
                             NH—CO
```

Barbituryl-5-acetic acid, CO CHCH$_2$COOH.—This acid was prepared by digesting one gram of the above sodium salt with 30 cc. of 20 per cent. hydrochloric acid. After concentration of the acid solution and cooling, the acid separated as light brown, hexagonal plates. It was purified by crystallization from boiling water and separated, on cooling, in plates which charred at 230° and then decomposed at 250° with effervescence. The acid occluded moisture and was dried for analysis at 125°.

	Calculated for $C_6H_6O_5N_2$	Found
N	15.05	15.13

The Action of Phosphorus Oxychloride on the Sodium Salt of Barbituryl-5-acetamide.—An attempt to condense this amide to a 1,3,9-pyrimazole, by means of this halide, was unsuccessful. Four and sixty-six hundreths grams of the dry salt were suspended in 30 cc. of phosphorus oxychloride and the mixture digested for 4 hours. The phosphorus halide had assumed a dark color and suspended in the fluid was a dark brown substance, which was apparently a mixture of the unaltered amide and sodium chloride. This was separated and the phosphorus oxychloride then evaporated, when a dark oily

residue was obtained. There was not, however, sufficient material for experimental purposes and, furthermore, a nitrogen determination indicated that it was not a definite substance. The product insoluble in the phosphorus oxychloride was dissolved in hot water, decolorized by digestion with bone coal and the solution concentrated. On cooling, well defined crystals, in the form of plates, separated and decomposed at about 248°–250° with violent effervescence. This substance was very soluble in hot and difficultly soluble in cold water. It was identified as barbituryl-5-acetic acid. A mixture of the substance with some of this acid melted at 248°–250°. Nitrogen determination (Kjeldahl) after drying at 125°:

	Calculated for $C_6H_6O_5N_2$	Found
N	15.05	15.24

The Condensation of Thiourea with Triethyl Ethane-α,α,β-tricarboxylate, $C_2H_5OOCCH_2CH(COOC_2H_5)_2$

Thiobarbituryl-5-acetamide, $\begin{array}{l} NH—CO \\ \vert \quad\quad \vert \\ CS \quad CHCH_2CONH_2.H_2O.— \\ \vert \quad\quad \vert \\ NH—CO \end{array}$

Three and eight-tenths grams of sodium were dissolved in 30 cc. of absolute alcohol and 3.1 grams of thiourea dissolved in the solution. Ten grams of the carboxylate were then added and the mixture warmed on the steam bath for 4.5 hours. The alcohol was then evaporated and the residue triturated with 30 cc. of cold water. A clear liquid was obtained, which separated in two distinct layers. These were carefully separated by means of a separatory funnel and each acidified with hydrochloric acid. No precipitate deposited from the upper layer and on evaporation only sodium chloride was obtained. From the lower layer, after acidifying and cooling, 3.1 grams of the amide were obtained. It was purified by dissolving in an excess of boiling water and then concentrating to a small volume and cooling, when it separated in the form of needles. This compound charred at 252° and then decomposed with effervescence when heated to 272°. It was dried for analysis at 100°.

Sulphur determination (Carius):
0.1694 gram substance gave 0.1835 gram $BaSO_4$.
Nitrogen determination (Kjeldahl):

	Calculated for $C_6H_7O_3N_3S.H_2O$	Found
S	14.67	14.8
N	19.18	19.04

In another experiment, in which we used 3.0 grams of sodium, 5.0 grams of thiourea and 14.0 grams of the carboxylic ester, the digestion was continued for only 2.5 hours, when the excess of alcohol was evaporated and the residue dissolved in an excess of water. On acidifying with concentrated hydrochloric acid, to avoid too great dilution, and cooling we obtained 2.0 grams of a substance which was difficultly soluble in water and insoluble in alcohol. This gave, after drying at 100°, 19.62 and 19.69 per cent. of nitrogen and decomposed at about 258° with effervescence. In order to purify this product it was finally dissolved in a large volume of water and the solution then concentrated and cooled, when thiobarbituryl-5-acetamide separated in the form of needles, and decomposed at 272° with effervescence. It was dried for analysis at 105°.

	Calculated for $C_6H_7O_3N_3S.H_2O$	Found I	Found II
N	19.18	19.00	18.87

In a third experiment the sodium salt of thiobarbituryl-5-acetamide and thiobarbituryl-5-acetic acid were isolated as follows: The condensation was effected as described in the previous experiment and the alcohol evaporated as usual. The solid residue was then dissolved in about 13 cc. of water, the solution concentrated and finally allowed to stand for several hours. The sodium salt separated in the form of long, colorless prisms which had no definite melting point. It was very soluble in water and separated from a concentrated solution in an anhydrous condition. Analysis (Kjeldahl):

	Calculated for $C_6H_6O_3N_3SNa$	Found
N	19.00	19.4

When the aqueous solution above, after filtration from the sodium salt, was acidified strongly with hydrochloric acid a

crystalline product separated. This dissolved in hot water, but on cooling the solution two distinct crystalline forms, needles and plates, were obtained. A nitrogen determination also indicated that we were not dealing with a definite substance but apparently a mixture of thiobarbituryl-5-acetamide and the corresponding acid. In order to obtain the pure acid the mixture was finally dissolved in 50 cc. of 20 per cent. hydrochloric acid and the solution concentrated to a small volume on the steam bath. The amide underwent hydrolysis by this treatment and, on cooling, *thiobarbituryl-5-acetic acid*,

$$\begin{array}{ll} NH & \!\!\!—CO \\ | & \;| \\ CS & \;CHCH_2COOH.2H_2O \\ | & \;| \\ NH & \!\!\!—CO \end{array}$$

separated in the form of needles. The acid contained two molecules of water of crystallization and decomposed with effervescence when heated above 230°.

Water determination:

0.6492 gram substance lost at 105° 0.0932 gram H_2O.

	Calculated for $C_6H_6O_4N_2S.2H_2O$	Found
H_2O	15.1	14.34

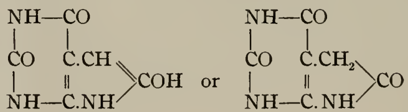
Nitrogen determination (Kjeldahl) in the anhydrous acid:

	Calculated for $C_6H_6O_4N_2S$	Found
N	13.86	13.86

The Condensation of Diethyl Cyanosuccinate, $C_2H_5OOCCH(CN)CH_2COOC_2H_5$, *with Urea*

This ester condenses normally with urea, forming a pyrimidine. The reaction, however, is not smooth and the yields of condensation products formed are small. Furthermore, it is extremely difficult to obtain consistent yields although the greatest care be taken to work under similar conditions. Secondary products are formed in small amount, which are difficult to separate. Of the several experiments which we carried out, we shall describe only two. These illustrate the nature of the reactions and the products formed.

Seven and five-tenths grams of the cyanosuccinic ester were condensed with urea (2.5 grams) by digestion in alcohol and in the presence of sodium ethylate (2.0 grams of sodium). After warming on the steam bath for about 16 hours the alcohol was then evaporated and the residue dissolved in 15 cc. of water. The fluid separated in two layers. The upper layer was acidified with hydrochloric acid and the solution concentrated but nothing but sodium chloride was obtained. The lower layer was likewise acidified with hydrochloric acid and allowed to stand, when a brownish colored powder deposited. This substance was insoluble in water, alcohol and glacial acetic acid. It dissolved in a cold, dilute sodium hydroxide solution and was reprecipitated unaltered by addition of hydrochloric acid. When heated in a capillary tube it began to darken at about 295°, but did not melt below 320°. Nitrogen determinations (Kjeldahl) agreed with the calculated value for *2,6,8-trioxy-1,3,9-pyrimazole*,



	Calculated for $C_6H_5O_3N_3$	Found I	Found II
N	25.15	25.5	25.16

After separation of the pyrimazole, the filtrate was acidified strongly with hydrochloric acid and then concentrated on the steam bath. On cooling barbituryl-5-acetic acid separated and was purified by crystallization from hot water. It separated in plates, which melted at 248°–250° with effervescence. Analysis (Kjeldahl):

	Calculated for $C_6H_6O_5N_2$	Found
N	15.05	15.07

The yields of the pyrimazole and the barbituryl-5-acetic acid were small.

In a second experiment 7 grams of the cyanosuccinate were condensed with 2.2 grams of urea by digestion for 5.5 hours. The alcohol was then evaporated and the residue dissolved in

20 cc. of water. This liquid formed two layers as described in the preceding experiment. These were carefully separated and acidified with hydrochloric acid. Only a small precipitate deposited from the upper layer, while from the lower layer a brown powder separated, which dissolved in hot water and deposited again on cooling. This substance did not melt below 338° and a nitrogen determination indicated that we were dealing with *4-iminobarbituryl-5-acetic acid*,

$$\begin{array}{lll} NH & — & CO \\ | & & | \\ CO & & CHCH_2COOH. \\ | & & | \\ NH & — & C:NH \end{array}$$

	Calculated for $C_6H_7O_4N_3$	Found
N	22.7	23.2

When the acid filtrate above was concentrated and cooled a crystalline substance separated, which was identified as barbituryl-5-acetic acid. It decomposed at 248°. A mixture of this product and some of the pure acid melted at the same temperature.

New Haven, Conn.
January 13, 1913

[Contributions from the Sheffield Laboratory of Yale University]

CCVI.—HYDANTOINS

THE ACTION OF AMMONIUM AND POTASSIUM THIOCYANATES ON α-AMINO ACIDS

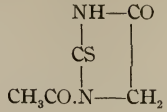
By Treat B. Johnson and Ben H. Nicolet

[TWENTY-FIRST PAPER]

It has been shown by one of us and his coworkers[1] that α-amino acids react with a thiocyanate in an acetic anhydride solution, in an unique manner, with formation of the corresponding 3-acetylthiohydantoins (I). Every α-amino monocarboxylic acid which we have examined has reacted in this manner. The transformation may be represented as follows:

[1] Johnson and Nicolet: J. Am. Chem. Soc., **33**, 1973. Johnson: J. Biol. Chem., **11**, 97. Johnson and Guest: This Journal, **47**, 242; **48**, 103. Johnson and O'Brien: J. Biol. Chem., **12**, 205.

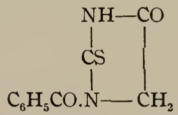
$$NH_2CH_2COOH + NH_4SCN + (CH_3CO)_2O \longrightarrow$$



(I)

It has also been shown that it is apparently a normal reaction for acyl derivatives of α-amino acids (II) also to react with thiocyanates, in the same medium, giving the corresponding acylthiohydantoins (III). The reaction with hippuric acid (II) may be represented as given below. This reaction, however, has received little attention, so far, because of pressure of other work, but it is now being investigated and will be applied to various acyclic and cyclic compounds containing the peptide grouping —$NH.CH_2.CO$—. The results will be published later.

$$\underset{\text{(II)}}{C_6H_5CONHCH_2COOH} + NH_4SCN + (CH_3CO)_2O \longrightarrow$$



(III)

During the progress of our investigation we had no reason to suspect that the nature of the inorganic thiocyanate would influence, to any extent, the course of these reactions. Komatsu[1] had previously applied the first reaction successfully with potassium thiocyanate and the two amino acids, glycocoll and alanine, but, as the writers[2] have already shown, he entirely misinterpreted the changes involved and consequently his conclusions were wrong. It was not until we found that our stock of Kahlbaum's ammonium thiocyanate was actually mislabeled potassium thiocyanate that we made the discovery[3] that these two salts do not react with the same readiness with α-amino acids under the conditions of our experiments. A

[1] Mem. Coll. Sci. Eng., Kyoto Univ. (Japan), **3**, 1 (1911).

[2] *Loc. cit.*

[3] Johnson: This Journal, **49**, 68.

repetition oi our work now reveals the fact that both salts combine with amino acids with formation of the same thiohydantoins, but, on the other hand, we find that the best yields, in every case so far examined, are obtained when the reactions are applied with ammonium thiocyanate.

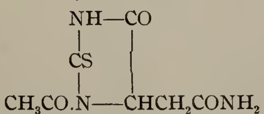
At present we shall not attempt to offer an explanation for this remarkable difference in the behavior of these two thiocyanates towards α-amino acids. Efforts will be made to obtain new data wh ch will enable us to draw more definite conclusions as to the mechanism of these changes. Furthermore, it is not improbable that, by the proper change of experimental conditions, thiohydantoins may be formed as well from potassium thiocyanate as by using the ammonium salt.

In the experimental part of this paper a description is given of the behavior of these two thiocyanates towards phenylalanine, asparagine, tyrosine, hippuric acid, alanine and pyrrolidonecarboxylic acid.

EXPERIMENTAL PART

In this investigation of the action of ammonium and potassium thiocyanates on α-amino acids the following proportions, unless otherwise stated, were always used, viz., two grams of the amino acid and 1.5–2.0 grams of the thiocyanate suspended in a mixture of 9 cc. of acetic anhydride and 1 cc. of acetic acid. These mixtures were then heated for 20 minutes on a steam bath, when, in every case, a clear solution was obtained. This was then poured into about 50 cc. of cold water in order to precipitate the acylhydantoin and the latter purified by recrystallization from alcohol or water.

The Conversion of Asparagine into 2-Thio-3-acetylhydantoin-4-acetamide[1]



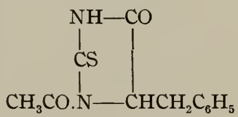
With Ammonium Thiocyanate.—With this reagent the formation of the acylthiohydantoin is very smooth. The liquid

[1] Johnson and Guest: THIS JOURNAL, **48**, 103. Johnson: *Loc. cit.*

assumes, on warming, a light yellow color and on pouring into water the thiohydantoin separates immediately as a yellow, crystalline substance. The crude hydantoin melted at 220° and the yield was 1.65 grams, or about 50 per cent. of the theoretical. The purified hydantoin melted at 223–224°.

With Potassium Thiocyanate.—The acetic anhydride solution of the amino acid amide was not colored strongly by heating with this salt and apparently there was little decomposition. The reaction, however, was not smooth. On pouring the liquid into water a clear yellow solution was obtained and no thiohydantoin separated after standing for 15 hours. After 24 hours about 0.2 gram of the hydantoin had separated, corresponding to a yield of about 6 per cent. The results were the same whether we used Kahlbaum's or Merck's potassium thiocyanate.

The Conversion of Phenylalanine into 2-Thio-3-acetyl-4-benzylhydantoin[1]



With Ammonium Thiocyanate.—The acylthiohydantoin is formed smoothly by the action of this salt on the amino acid. The acetic anhydride solution assumes a light yellow color on warming, and on pouring into water the hydantoin separates as an oil, which soon crystallizes. The yield of crude hydantoin is generally about 2.8 grams, or 94 per cent. of the theoretical.

With Potassium Thiocyanate.—When this salt was employed an oil was obtained by pouring into cold water, which partially solidified after standing 15 hours. The yield of crude material was 2.2 grams. This hydantoin was purified by crystallization from boiling alcohol and separated, on cooling, in colorless prisms or hexagonal plates. The compound melts at 170° to a clear oil instead of 257° as erroneously given in our previous paper.[2] The hydantoin is difficultly soluble in water and is

[1] Johnson and O'Brien: J. Biol. Chem., **12**, 205. Johnson: *Loc. cit.*

[2] Johnson and O'Brien: *Loc. cit.*

transformed quantitatively by hydrolysis with hydrochloric acid into the thiohydantoin of phenylalanine melting at 185°.

The Conversion of Tyrosine into 2-Thio-4-(p-*hydroxybenzyl*)-*hydantoin*

```
NH—CO
|    |
CS   |
|    |
NH—CHCH2C6H4OH
```

With Ammonium Thiocyanate.—In this experiment 2.0 grams of Kahlbaum's active tyrosine and 2.0 grams of the thiocyanate were suspended in a mixture of 30 cc. of acetic anhydride and 1 cc. of glacial acetic acid and the mixture then heated on the steam bath until a clear solution was obtained. On cooling, nothing separated and on pouring into cold water an oil deposited, which dissolved again on warming gently. The clear aqueous solution was then evaporated, when we obtained apparently the acylthiohydantoin as a viscous oil, which was extremely soluble in water and showed no signs of crystallizing after long standing. The crude product was dissolved in hydrochloric acid and the solution evaporated on the steam bath, when we obtained the tyrosinethiohydantoin in a crystalline condition. The yield was 2.0 grams, or 82 per cent. of the theoretical. This thiohydantoin is soluble in about 10 parts of hot water, and separates from this solvent, on cooling, in yellow needles melting at 211° without apparent decomposition. After repeated recrystallizations the compound can be obtained nearly colorless. It is readily soluble in 95 per cent. alcohol.

Analysis (Kjeldahl):

	Calculated for $C_{10}H_{10}O_2N_2S$	Found
N	12.60	12.41

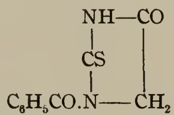
The thiohydantoin is soluble in 5 per cent. potassium hydroxide solution, and on acidifying the solution it is recovered unaltered and melting at 211°.

With Potassium Thiocyanate.—We used in this experiment 1 gram of tyrosine, 0.7 gram of potassium thiocyanate, 10 cc.

of acetic anhydride and 0.7 cc. of glacial acetic acid. Otherwise the procedure was the same as described in the previous experiment. The anhydride solution assumed no red color during the heating and there was no evidence of decomposition, but after pouring into water and subjecting to hydrolysis with hydrochloric acid, we obtained only 0.2 gram of tyrosinethiohydantoin. Therefore, in this case also the best results are obtained when the reagent used is ammonium thiocyanate.

Desulphurization of Tyrosinethiohydantoin.—Seventy-five hundredths gram of the thiohydantoin was desulphurized by boiling for 1.5 hours with a solution of 4 grams of chloroacetic acid in 5 cc. of water. On cooling, 0.6 gram of the hydantoin of tyrosine separated and melted at 262° with slight effervescence.[1]

The Formation of 2-Thio-3-benzoylhydantoin from Hippuric Acid[2]



This thiohydantoin is formed by the action of either ammonium thiocyanate or potassium thiocyanate on hippuric acid in acetic anhydride solution. The yields of hydantoin obtained are, however, decidedly different. In the case of the ammonium salt the reaction is very smooth and the yield of hydantoin generally averages about 85–88 per cent. of the theoretical. In fact, the thiohydantoin separates almost immediately in a crystalline condition after pouring the anhydride solution into cold water and is nearly pure after one recrystallization from alcohol. On the other hand, by using the potassium salt the formation of the thiohydantoin is far less smooth and we have never succeeded in obtaining a yield of this compound greater than 50 per cent. of the calculated amount. We have used different specimens of potassium thiocyanate and acetic anhydride, but, in every case when we

[1] Wheeler and Hoffman: THIS JOURNAL, **45**, 368.
[2] Johnson and Nicolet: *Loc. cit.*

used this salt, the anhydride solution always assumed a deep red color within a few minutes and if heated longer than 30 minutes it generally became opaque. On pouring into water, after the reaction was complete, the thiohydantoin generally is obtained very impure and separates as a dark, heavy oil, which crystallizes only after long standing. The purity of the hydantoin is also influenced by the length of time of heating. We find that the reaction proceeds slowly at ordinary temperature (20°–30°), but even when conducted under these conditions the yield is only about 50 per cent. of that obtained by using ammonium thiocyanate. In order, therefore, to prepare this thiohydantoin in quantity from hippuric acid it is necessary to use ammonium thiocyanate and the following procedure is recommended for its separation: Suspend 2.0 grams of hippuric acid (pulverized) and 1.25 molecular proportions of dry ammonium thiocyanate in a mixture of 9 cc. of acetic anhydride and 1 cc. of glacial acetic acid and connect the flask with a return condenser. Then heat on the steam bath at 90°–100° until the hippuric acid and ammonium salt completely dissolve and the solution assumes an orange color. This requires about 20 minutes' heating. The anhydride solution is then cooled and poured into about 5 parts of cold water and the mixture stirred, when the hydantoin will generally crystallize immediately. This product is very pure, has a light yellow color and needs no further purification before conversion into the 2-thiohydantoin, $NH.CS.NH.CH_2.CO$, by hydrolysis with hydrochloric acid. The benzoyl group is easily removed by boiling with hydrochloric acid and then evaporating to dryness. The crystalline residue is then triturated with ether to dissolve benzoic acid and the 2-thiohydantoin purified by crystallization from alcohol. By application of this reaction it is possible to obtain the thiohydantoin in any amount desired. This can also be converted into hydantoin by desulphurization with chloroacetic acid.

2-Thio-3-acetyl-4-methylhydantoin from Alanine[1]

With Ammonium Thiocyanate.—The formation of the

[1] Johnson: *Loc. cit.*

hydantoin is very smooth, when this thiocyanate is used, and the yield is excellent. The hydantoin separates immediately on pouring the acetic anhydride solution into water and generally melts without further purification at 166° to an oil.

With Potassium Thiocyanate.—When this salt is used there is no apparent indication that the reaction is abnormal while heating the anhydride solution at 90°–100°. The thiocyanate dissolves completely and the liquid assumes no color. The hydantoin, however, is not obtained in good yield. On pouring the anhydride solution into cold water the hydantoin first separates as a heavy oil, which finally solidifies. The weight of the crude product was only 1.3 grams, or about 34 per cent. of the theoretical.

The Action of Thiocyanates on Pyrrolidonecarboxylic Acid

Any derivative of this cyclic acid which is characteristic and suitable for its identification is of interest because of the probability that pyrrolidonecarboxylic acid is one of the constituents of protein.[1] A derivative of this character is the corresponding thiohydantoin, which has been described in a previous paper from this laboratory.[2] It is formed by the action of ammonium thiocyanate on this acid and also, but in small amount only, by the action of the potassium salt. If the potassium salt is used and the experiment is conducted under the conditions outlined in the introduction to the experimental part of this paper a product is formed which is very impure and enough of the hydantoin cannot be obtained for experimental purposes. On the other hand, with ammonium thiocyanate the product is crystalline and there is no difficultly in obtaining good yields. This hydantoin crystallizes from water or alcohol in prismatic crystals which melt at 206°.

New Haven, Conn.
January 13, 1913

[1] Abderhalden and Wurm: Z. physiol. Chem., **82**, 160.
[2] Johnson and Guest: *Loc. cit.*

CONCERNING POTASSIUM β-FERRICYANIDE

By H. L. Wells

Hauser and Biesalski[1] have recently attempted to show that the isomeric form of potassium ferricyanide described by Locke and Edwards[2] is merely the ordinary salt contaminated with a little colloidal Prussian blue.

Since the investigation of Locke and Edwards was made in this laboratory, and since these gentlemen are no longer engaged in chemical research, I am taking occasion to show that Hauser and Biesalski are entirely mistaken in regard to this matter.

Hauser and Biesalski appear to assume that the only differences between the α- and β-ferricyanides in their reactions with the salts of the heavy metals are slight variations in the colors of the precipitates. This is absolutely incorrect, as they ignore several important reactions, particularly the one with a dilute nitric acid solution of bismuth nitrate, which was mentioned repeatedly and very prominently in the articles of Locke and Edwards, and was used by them as the principal means of testing the purity of their preparations of β-ferricyanide.

I have found one of the original preparations of potassium β-ferricyanide, made by Locke and Edwards, which has been kept here for about 13 years. It still gives a practically clear solution with water, and the solution gives no precipitate with bismuth nitrate, while ordinary potassium ferricyanide gives an immediate precipitate, even in very dilute solutions.

This reaction alone is sufficient to show that Hauser and Biesalski are absolutely wrong in their conclusions, for it is inconceivable that the presence of a minute amount of colloidal Prussian blue should prevent the formation of an exceedingly slightly soluble precipitate, and, moreover, Locke and Edwards found this reaction to furnish a delicate test for the ordinary ferricyanide in the presence of large amounts of the isomer.

It is to be noticed also that Hauser and Biesalski make no mention of the fact that Locke and Edwards found the β-ferri-

[1] Ber. d. chem. Ges., **45**, 3516 (1912).

[2] This Journal, **21**, 193, 413.

cyanide to contain a molecule of water of crystallization. They assume that the presence of a trace of Prussian blue is capable of modifying the habit of the crystals, but it is impossible to imagine that this minute quantity of colloidal substance, which they estimate as amounting to "0.001 Mole auf 1 Mol Ferricyankalium," should be capable of causing the addition of water of crystallization to the main substance.

The recent important work of Bellucci and Sabatini,[1] who have shown that the α- and β-ferricyanides are nitrile and isonitrile forms, is mentioned by Hauser and Biesalski as furnishing the only chemical evidence of the existence of two different modifications of potassium ferricyanide. This is not true, since Locke and Edwards found numerous chemical distinctions, among which are the bismuth reaction and the difference in water of crystallization, which have already been discussed.

It appears, however, that Hauser and Biesalski have confirmed the results of Bellucci and Sabatini as well as could be expected in view of the apparent circumstance that, in being ignorant of the bismuth test, they were not in a position to prepare pure potassium β-ferricyanide. They admit that the formation of ferric imido ester proceeds more smoothly with ordinary potassium ferricyanide than with the form "contaminated with Prussian blue," although they think that this difference is due to a catalytic action of the impurity. Their statement that the ester may be produced, although in much smaller quantity, from the "second form" of the ferricyanide is not worthy of serious consideration, since it appears that they knew no method of testing the β-ferricyanide for the original salt, which, as Locke and Edwards have shown, is an impurity that is avoided with difficulty.

There seems to be no excuse for the evident ignorance on the part of Hauser and Biesalski of important features in the work of Locke and Edwards, for they refer to the original articles, and, since they are situated at the University of Berlin, these articles were certainly easily accessible to them.

SHEFFIELD LABORATORY, NEW HAVEN, CONN.
January, 1913

[1] Atti accad. Lincei, **23**, I, 176.

A STUDY OF THE CONDUCTIVITY, DISSOCIATION AND TEMPERATURE COEFFICIENTS OF CONDUCTIVITY OF CERTAIN INORGANIC SALTS IN AQUEOUS SOLUTION, AS CONDITIONED BY TEMPERATURE, DILUTION, HYDRATION AND HYDROLYSIS

By E. J. Shaeffer and Harry C. Jones

The work described in this paper is but a part of the systematic study of the conductivity, dissociation and temperature coefficients of conductivity of electrolytes which was begun in this laboratory twelve years ago in connection with the solvate theory of solution proposed by Jones.[1] We have studied, in this investigation, inorganic salts by the modified Kohlrausch conductivity method, and in interpreting the results we shall make use of what is known regarding the nature of solution. The theory of electrolytic dissociation,[2] the solvate theory of Jones,[3] the relation pointed out by Dutoit and Aston,[4] connecting the association of a solvent with its dissociating power, and the Thomson[5]-Nernst[6] hypothesis bringing out the relations between dissociating power and dielectric constant of the solvent, enable us to explain satisfactorily a very large part of the conductivity data obtained in this investigation.

HISTORICAL REVIEW

Jones and his coworkers,[7] in discussing conductivity measurements, have given satisfactory reviews of the conductivity work done previous to that carried out in this laboratory. In this review only the work bearing on the conductivity of inorganic compounds in aqueous solutions will be considered. The systematic study of the nature of inorganic salts in aqueous solution and their dissociation as measured by the modified

[1] This Journal, **23**, 89 (1900).
[2] Z. physik. Chem., **1**, 631 (1886).
[3] This Journal, **23**, 103 (1900).
[4] Compt. rend., **125**, 540 (1899).
[5] Phil. Mag., **36**, 320 (1894).
[6] Z. physik. Chem., **13**, 531 (1894).
[7] This Journal, **34**, 358 (1905); **40**, 355 (1908); **46**, 240 (1911); **48**, 500 (1912).

Kohlrausch conductivity method was begun by Jones and West in 1904.

It was known that conductivity increased with dilution and rise in temperature, and that the dissociation of electrolytes at high temperatures decreased with rise in temperature, but not much of a reliable nature was known regarding the change in dissociation of electrolytes over the lower temperature ranges with rise in temperature. It was also known that dissociation increased with increase in dilution up to a certain point, where it was complete. For salts, temperature coefficients of conductivity were shown to increase with rise in temperature, while for acids but little change with rise in temperature manifested itself. Satisfactory explanations for most of these facts were lacking. Moreover, the literature contained but a small amount of reliable data regarding the dissociation of important inorganic acids and salts over wide ranges of temperature and dilution. One of the objects in undertaking the investigation was to supply these important data.

Confidence in conductivity methods was greatly strengthened by the work of Jones and West.[1] They did much to improve the accuracy of conductivity measurements. Dissociation over a range of temperature from 0°–35° was found to decrease with rise in temperature. This they pointed out was in accordance with the relation of Dutoit and Aston,[2] connecting the association of a solvent with the dissociation of the dissolved substance. Ramsay and Shields[3] had already pointed out that the association of a solvent decreased with rise in temperature. This result was in accord with the work of von Willer[4] and the Thomson[5]-Nernst[6] hypothesis, which showed that the dissociating power of a solvent increased with its dielectric constant, and that the effect of rise in temperature was to decrease the dielectric constant of the solvent. They found that the percentage temperature coefficients of conductivity

[1] This Journal, **34**, 357 (1905).
[2] Compt. rend., **125**, 240 (1897).
[3] Z. physik. Chem., **12**, 433 (1893).
[4] Phil. Mag., [6] **7**, 655 (1904).
[5] *Ibid.*, **36**, 320 (1894).
[6] Z. physik. Chem., **13**, 531 (1894).

decreased with rise in temperature, and that the temperature coefficients of conductivity, in the case of salts, increased with rise in temperature, while for acids they decreased.

The work of Jones and his coworkers had already proved that a large number of compounds were hydrated in aqueous solutions, and in Monograph No. 60 of the Publications of the Carnegie Institution of Washington are recorded the approximate compositions of a large number of hydrates. With these conceptions in mind, Jones[1] pointed out a number of relations between conductivity, temperature coefficients of conductivity and the present hydrate theory. Since most ions are hydrated in aqueous solutions, with rise in temperature these unstable hydrates would break down. The effect would be to decrease the mass of the ion, and since the viscosity of the solutions studied changed but slightly with rise in temperature, and the driving power of the current was but little increased, the decreasing mass of the ion is the chief factor in conditioning the increase in conductivity with rise in temperature. It was pointed out that, due to the greater complexity of the hydrates at higher dilutions, we should expect them to change more at high than at low dilutions with rise in temperature. This explains the fact that temperature coefficients of conductivity are greater at high than at low dilutions, and also why the increase in the value of the coefficient is greatest for those substances that have the greatest hydrating power. Jones and Pearce[2] called attention to the fact that the hydrating power of a salt is primarily a function of the cation, and that its ability to hydrate is an inverse function of its atomic volume. Before this relation was pointed out, it was difficult to see how the potassium, rubidium and caesium ions with large atomic volumes could have larger migration velocities than the sodium ions of smaller mass and atomic volume.

Jones and Jacobson[3] continued the work of West. They improved earlier methods and obtained results which substantiated those noted by Jones and West. The effect of

[1] This Journal, **35**, 445 (1906).
[2] *Ibid.*, **38**, 736 (1907).
[3] *Ibid.*, **40**, 355 (1908).

hydrolysis, acting so as to vitiate the true value of $\mu\infty$, was mentioned. They, furthermore, concluded that salts which are strongly hydrated in solution show a greater increase in conductivity with rise in temperature than salts which are slightly hydrated.

Having these facts in mind, Clover and Jones[1] continued the study of the problem, working at temperatures ranging from 35°–80°. They made it possible to determine conductivities to a temperature as high as 65°. Certain difficulties, such as the solubility of glass and changes in the cell constants, were overcome. They concluded that it is not practical to measure the conductivity of a solution at 80° unless its concentration is around 0.01 N. The relations pointed out at lower temperatures were also found to hold at higher temperatures. From these results and previous ones, it was now clearly seen that substances with equal hydrating power have approximately the same temperature coefficients of conductivity. As conductivity depends largely on the complexity of the hydrate formed by the ions, we should expect this to be true from the hydrate theory. The sulphates were excepted from the above conclusion, because they are largely polymerized in aqueous solutions. At these temperatures, it was found that dissociation decreased slightly with rise in temperature.

West and Jones[2] continued the work at these high temperatures. They improved still further the methods of measuring conductivity at high temperatures, and obtained results very similar to those found by Clover and Jones.

Hosford and Jones[3] worked at temperatures ranging from 0°–65°. The effect of hydrolysis as causing abnormally great conductivity was pointed out, and it was stated that hydrolysis increases both with dilution and rise in temperature. The effect of hydrolysis on the green variety of chromic salts was shown to be less than on the violet form when the dilution increases. It was suggested that the abnormally rapid increase in conductivity is often caused by a decrease in polymerization. The con-

[1] This Journal, **43**, 508 (1910).
[2] *Ibid.*, **44**, 508 (1910).
[3] *Ibid.*, **46**, 240 (1911).

ductivity of double salts at temperatures ranging from 0°–65° was found to be less than the sum of the conductivities of the constituent salts, as had been pointed out by Jones and his coworkers[1] at 25°.

Miss Winston and Jones[2] extended the work already done at low temperatures, and their results confirmed those earlier obtained. To account for the increase in percentage dissociation of certain salts with rise in temperature, and large temperature coefficients where there is no reason to expect large hydration, the view that inductive action takes place through the solvent between charged ions and neutral molecules, giving rise to complex ions and molecules in solutions, was advanced by Miss Winston.[2]

The investigation of Howard and Jones[3] continued the work done at higher temperatures. A time factor of hydrolysis was noted, and its effect on conductivity measurements pointed out. This review brings the work up to the present.

Since the beginning of this work, complete conductivity data for 110 of the more common inorganic compounds have been carefully worked out over wide ranges of dilution and temperature. The work has also been extended to about 90 of the more common organic acids. A good idea of the scope of this work may be obtained from a recent publication by Jones[4] and his coworkers in which all the best data obtained thus far have been tabulated and discussed.

PURPOSE OF THIS INVESTIGATION

The object in carrying out this work was to accumulate more data in regard to the dissociation of electrolytes over wide ranges of temperature and dilution, to improve and study the well known Kohlrausch conductivity method as a means of measuring dissociation, to test more fully the conclusions already reached by investigators in this laboratory and to discover new relations from the data obtained.

[1] This Journal, **19**, 83 (1897); **22**, 5 (1899); **22**, 110 (1899); **25**, 349 (1901).
[2] *Ibid.*, **46**, 368 (1911).
[3] *Ibid.*, **48**, 500 (1912).
[4] Carnegie Institution of Washington, Publication No. **170**.

EXPERIMENTAL DISCUSSION

Apparatus

The Bridge.—About half of the conductivity readings for the lower temperature work were taken from a straight slide wire Wheatstone bridge, calibrated by the method of Strouhal and Barus.[1] The remainder of the work at lower temperatures and all of the work at higher temperatures was done with an improved circular slide wire bridge, made by Leeds and Northrup. By means of this bridge, it was possible to read the resistance of the solution down to fractions of a millimeter.

Rheostat.—The resistance box was standardized against a rheostat which, in turn, had been standardized by the Bureau of Standards in Washington. Considerable stress should be laid upon the necessity of keeping all connections absolutely clean, especially the plugs of the rheostat. The usual methods of cleaning the connections are far from sufficient.

It was found that unless the wires connecting the cells and rheostat were short and of a large diameter, very appreciable errors were introduced in measuring the resistances of concentrated solutions.

Cells.—The cells were of the general types which have been in use in this laboratory for some time. They have recently been described and sketched.[2] As a rule, eight dilutions of each salt were studied, and for each dilution there was a cell the distance between whose electrodes was so arranged that clear minima could be obtained on the bridge. The nine cells had done long service at both high and low temperatures, and from tests it was concluded that practically all soluble matter had been removed from them when heated to temperatures as high as 65°.

During the course of this investigation thirty-five inorganic salts were studied, and the cell constants were taken twenty-three times. No difficulty at all was experienced in keeping the electrode distance of the cells constant for the temperature range 0°–35°. Clover and Jones[3] and West and Jones[4]

[1] Wied. Ann., **10,** 32 (1880).

[2] Carnegie Institution of Washington, Publication No. **170,** p. 5.

[3] This Journal, **43,** 195 (1910).

[4] *Ibid.*, **44,** 511 (1910).

experienced difficulty in keeping the electrode distance of the cells constant for the temperature range 35°–65°. Their recommendations were carefully adhered to. At the very beginning of the work at high temperatures, the cell constants were found to undergo change. It was caused, in our opinion, by forcing the ground glass stoppers too tightly into the cell cups. At 50° and 65°, the accumulated pressure would at times force the stoppers out of the cells, and invariably the electrode distance was disturbed. This was easily overcome by loosely stoppering the cells, and the work done at this period was repeated.

The cell constants were always determined at 25°. To determine the constants of the four cells with the greatest electrode distance, a 0.02 N potassium chloride solution was used. Its conductivity was taken as 129.7. To determine the constants of the remaining four cells, a 0.002 N solution of potassium chloride was used. Its conductivity value was determined several times and always found to be close to 135.5 For the water cell a 0.001 N potassium chloride solution was used. Its conductivity was usually close to 140.

Baths.—The baths used to maintain constant temperature were of the type described by Jones.[1] For the higher temperature work, an efficient cover was devised[2] which served to keep the temperature of the air above the cells at about the same temperature as the water surrounding the cells. During conductivity measurements the water contained in the bath was actively stirred by means of a hot air engine. The thermometers were carefully calibrated against standard ones. During part of the work, the temperature of the baths was regulated by means of thermoregulators similar to the type devised by Reid.[3] For the most part, however, the temperatures were regulated by hand.

Containing Vessels.—All flasks and burettes were calibrated and recalibrated by the method of Morse and Blalock.[4] In addition, the 1000 cc. and 500 cc. flasks used to measure

[1] Carnegie Institution of Washington, Publication No. **170**, p. 9.

[2] This Journal, **48**, 504 (1912).

[3] *Ibid.*, **41**, 148 (1909).

[4] *Ibid.*, **16**, 479 (1894).

the volume of the mother solution were calibrated also by the weight method, and very close agreements with the method of Morse and Blalock were obtained. For the higher temperature work, all containing vessels were of Jena glass. How slightly soluble this glass is will be brought out in a later connection. The 500 cc. flask used for this work was calibrated so that when it was filled to the proper mark at 20° it would contain 500 cc. of solution at 50°.[1]

Preparation of Solutions.—Whenever a salt was used at both high and low temperatures, two sets of solutions were prepared. The conductivities of both sets were determined at 35°, and thus a check upon our work was obtained. The solutions used for the lower temperature work were made up at 20°.

Since the volume changes of a solution are so great with change in temperature, we are obviously at a great disadvantage in making up solutions at temperatures very far removed from that of the room. At high temperatures, it is a well known fact that the solubility of the glass is another factor which must be taken into account. Methods described by West and Jones[2] and by Springer and Jones[3] made it possible to prepare solutions at 20° and to use these solutions for conductivity determinations at 35°, 50° and 65°.

For the high temperature work, the solutions were made up from a mother solution contained in a specially calibrated 500 cc. flask. This flask had two marks. To determine the position of the lower mark the weight of 500 cc. of distilled water at 50°, air displacement being taken into account, was used. When this flask was filled with a solution up to the mark at 20° and then warmed to 50° we had just 500 cc. at 50°. To test the correctness of the above mark, the flask was calibrated by the method of Morse and Blalock so as to contain 500 cc. at 50°. Of course, the proper corrections for these calibrations were taken into account. When a solution at 20° was added to the flask up to the 20° mark and heated to 50°, it was found

[1] This Journal, **48**, 417 (1912).
[2] *Ibid.*, **44**, 508 (1910).
[3] *Ibid.*, **48**, 416 (1912).

that its meniscus corresponded with the calibration mark at 50° determined by the method of Morse and Blalock. With but very few exceptions, the coefficients of expansion of our most concentrated solutions were only slightly different from that of distilled water. We were thus assured that our solutions, made up at 20°, would be of the proper concentration when heated to 50°. To correct for the increase in concentration due to cooling such a solution down from 50° to 35°, the factor 0.994, as worked out by Jones and Clover,[1] was multiplied into all conductivity values obtained at 35°. The factor 1.0076,[2] when multiplied into the conductivities obtained at 65°, corrected for the decrease in concentration due to warming the solutions from 50° to 65°.

Purification of Salts.—Nearly every salt worked with in this investigation came from Kahlbaum. Just how each salt was purified and the concentration of the mother solution determined is stated above the conductivity tables for that particular salt. It is desirable to do this in some detail, since conductivity data obtained by different investigators for the same substance are often discordant, and unless the investigator makes known the method of purification, and the way in which the concentration of the mother solution was ascertained, it is difficult to tell which values are more likely to be correct. Such information is certainly of great assistance to other investigators in this field.

Conductivity Water.—All the water used in this work was purified by the method of Jones and Mackay.[3] The water thus obtained had an average conductivity of 0.7×10^{-6} at 0°.

The conductivity data are expressed in Siemens units according to well known methods of calculation.[4] Each conductivity value recorded is the average of three readings.

Ammonium Hydrogen Sulphate

The above salt was recrystallized from conductivity water. The exact strength of the mother solution was determined

[1] This Journal, **43**, 187 (1910).
[2] *Ibid.*, **44**, 510 (1910).
[3] *Ibid.*, **19**, 91 (1897).
[4] Carnegie Institution of Washington, Publication No. **170**, p. 11.

by precipitation of the sulphuric acid by means of barium chloride.

Table I.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
2	207.2	35.9	223.8	31.4	235.3	27.5
8	263.5	45.6	286.0	40.1	303.2	35.5
32	339.2	58.8	374.2	52.5	396.5	46.4
128	433.9	75.2	485.9	68.2	525.3	61.4
512	510.2	88.4	593.5	83.3	666.1	77.9
1024	543.9	94.2	647.1	90.8	794.5	93.0
2048	560.0	97.0	681.5	95.6	820.6	96.0
4096	577.2	100.0	712.5	100.0	855.2	100.0

Table II.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	1.11	0.54	0.77	0.34
8	1.50	0.57	1.15	0.40
32	2.33	0.69	1.49	0.40
128	3.47	0.80	2.63	0.54
512	5.55	1.08	4.84	0.82
1024	6.88	1.26	9.83	1.52
2048	8.10	1.25	9.27	1.36
4096	9.02	1.56	8.85	1.23

Tetraethylammonium Iodide

The mother solution was standardized by weighing the dry and purified salt.

Table III.—Conductivity

V	0°	12°.5	25°	35°
8	38.6	54.6	72.8	88.5
32	46.5	65.4	86.8	105.0
128	51.1	72.1	95.4	114.8
512	52.8	73.9	98.0	118.4
1024	53.3	75.2	99.3	119.7
2048	54.4	77.0	101.7	122.5
4096	54.0	76.5	101.6	122.9

Table IV.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.28	3.31	1.46	2.67	1.57	2.15
32	1.51	3.25	1.70	2.60	1.82	2.09
128	1.67	3.29	1.86	2.56	1.94	2.03
512	1.69	3.20	1.92	2.59	2.04	2.08
1024	1.76	3.20	1.93	2.58	2.04	2.07
2048	1.78	3.27	1.98	2.57	2.08	2.04
4096	1.80	3.32	2.00	2.61	2.12	2.08

Table V.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	70.9	70.9	71.6	72.0
32	85.5	84.9	85.3	85.4
128	93.1	93.6	93.7	93.4
512	97.1	95.9	96.3	96.3
1024	98.0	97.7	97.6	97.5
2048	100.0	100.0	100.0	99.7
4096	99.2	99.4	99.9	100.0

Ammonium Sodium Hydrogen Phosphate

It was found that concentrated solutions of this salt decomposed at about 25°. For that reason it could not be safely purified by ordinary methods. The phosphoric acid in the mother solution was determined by means of magnesia mixture.

Table VI.—Conductivity

V	0°	12°.5	25°	35°
8	65.6	...	...	...
32	84.4	119.2	158.7	186.5
128	96.5	136.7	181.4	216.6
512	100.7	141.4	186.4	221.6
1024	104.7	145.7	193.6	235.2
2048	103.9	144.7	190.9	229.2

Table VII.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	2.78	3.30	3.16	2.65	2.78	1.49
128	3.21	3.32	3.57	2.61	3.52	1.62
512	3.26	3.24	3.60	2.54	3.52	1.58
1024	3.36	3.22	3.83	2.62	4.16	1.76
2048	3.36	3.22	3.70	2.55	3.83	1.67

Table VIII.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	62.6	...	...	...
32	80.6	81.7	81.9	79.3
128	91.3	93.1	93.7	92.1
512	96.3	97.0	96.2	94.2
1024	100.0	100.0	100.0	100.0
2048	99.2	99.3	98.6	97.4

Sodium Chloride

This salt was twice recrystallized from concentrated solutions by the addition of purified hydrochloric acid gas. It was then dried in an air bath for six hours at about 260°.

Table IX.—Conductivity

V	0°	12°.5	25°	35°
2	48.1	66.4	86.5	104.2
8	53.5	74.7	98.5	118.5
32	57.5	80.6	106.8	129.5
128	60.4	84.9	112.6	136.3
512	62.3	87.8	116.4	141.2
1024	61.6	86.9	115.4	140.0

Table X.—Temperature Coefficients

	0–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.46	3.04	1.61	2.44	1.77	2.05
8	1.70	3.19	1.90	2.54	2.00	2.03
32	1.85	3.21	2.09	2.59	2.27	2.12
128	1.96	3.24	2.21	2.60	2.37	2.11
512	2.04	3.27	2.29	2.61	2.48	2.13
1024	2.02	3.28	2.28	2.62	2.46	2.13

Table XI.—Percentage Dissociation

V	0°	12°.5	25°	35°
2	77.2	75.6	74.4	73.8
8	85.9	85.1	84.6	83.9
32	92.3	91.8	91.7	91.6
128	96.9	96.7	96.6	96.5
512	100.0	100.0	100.0	100.0
1024	98.9	99.0	99.1	99.1

Sodium Chlorate

The purified salt was dried in an air bath for two hours at 110°.

Table XII.—Conductivity

V	0°	12°.5	25°	35°
2	41.6	57.5	74.7	90.0
8	47.4	66.1	86.7	104.4
32	51.7	72.4	95.0	115.2
128	54.7	76.9	101.1	122.5
512	56.0	78.9	104.6	127.0
1024	56.2	79.0	104.1	126.3
2048	56.1	78.8	104.1	125.8

Table XIII.—Temperature Coefficients

V	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.27	3.05	1.38	2.40	1.53	2.04
8	1.50	3.12	1.66	2.41	1.77	2.05
32	1.66	3.21	1.80	2.49	2.02	2.12
128	1.78	3.25	1.94	2.53	2.14	2.12
512	1.83	3.26	2.05	2.64	2.36	2.25
1024	1.82	3.24	2.01	2.54	2.22	2.13
2048	1.81	3.22	2.02	2.56	2.17	2.09

Table XIV.—Percentage Dissociation

V	0°	12°.5	25°	35°
2	74.0	72.8	71.4	70.8
8	84.3	83.6	82.9	81.4
32	91.9	91.6	90.8	90.7
128	97.3	97.3	96.6	96.4
512	99.6	99.8	100.0	100.0
1024	100.0	100.0	99.5	99.5
2048	99.7	99.7	99.5	99.0

Sodium Chlorate

The purified salt was dried in an air bath for two hours at 110.°

Table XV.—Conductivity and Dissociation

V	35°		50°		65°	
	μ_v	α	μ_v	α	μ_v	α
8	103.7	79.5	132.1	78.5	164.4	77.7
32	118.0	90.4	151.6	90.0	186.3	88.1
128	122.9	94.2	158.4	94.1	198.7	94.0
312	126.1	96.6	165.2	98.1	204.4	96.7
1024	130.2	99.8	167.8	99.6	211.3	100.0
2048	130.5	100.0	168.3	100.0	209.1	99.0

Table XVI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.90	1.89	2.15	1.62
32	2.24	1.94	2.31	1.52
128	2.39	1.94	2.68	1.69
512	2.54	2.00	2.61	1.58
1024	2.51	1.93	2.90	1.78
2048	2.52	1.93	2.72	1.62

Sodium Perchlorate

After being recrystallized, the purified product was dried to constant weight in a weighing tube at 140°. The weighing tube was used because the salt was found to be somewhat deliquescent.

Table XVII.—Conductivity

V	0°	12°.5	25°	35°
8	49.5	69.0	90.3	109.1
32	53.5	74.9	98.5	119.2
128	56.3	78.9	104.2	126.1
512	57.0	80.0	105.7	128.8
1024	59.6	83.6	109.2	132.6
2048	60.01	84.4	111.5	135.4
4096	60.05	85.9	114.3	139.1

Table XVIII.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.56	3.15	1.70	2.46	1.88	2.08
32	1.71	3.18	1.88	2.51	2.07	2.10
128	1.81	3.21	2.02	2.56	2.19	2.10
512	1.83	3.21	2.05	2.56	2.31	2.18
1024	1.92	3.24	2.05	2.45	2.34	2.14
2048	1.95	3.25	2.17	2.57	2.39	2.14
4096	2.07	3.44	2.27	2.65	2.48	2.17

Table XIX.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	82.4	80.3	79.0	78.4
32	89.1	87.2	86.2	85.7
128	93.7	91.8	91.1	90.7
512	98.6	95.2	94.4	92.6
1024	99.2	97.3	95.5	95.3
2048	99.9	98.2	97.5	97.4
4096	100.0	100.0	100.0	100.0

Sodium Perchlorate

The mother solution for this series was prepared in exactly the same way as that for the series at lower temperatures. The specimen of salt used was not the same as that used for the lower temperature work.

Table XX.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
8	109.3	80.9	139.6	80.2	171.5	79.9
32	119.1	88.2	152.4	87.6	187.6	87.4
128	125.5	93.0	160.7	92.4	198.4	92.4
512	129.5	95.9	166.7	95.8	205.9	95.9
1024	132.0	97.8	170.4	97.9	211.3	98.4
2048	133.8	99.1	170.6	98.0	212.5	99.0
4096	135.0	100.0	173.9	100.0	214.6	100.0

Table XXI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.02	1.85	2.13	1.53
32	2.22	1.86	2.35	1.54
128	2.35	1.87	2.51	1.59
512	2.48	1.91	2.61	1.57
1024	2.56	1.94	2.73	1.60
2048	2.45	1.83	2.79	1.63
4096	2.59	1.92	2.71	1.56

Disodium Hydrogen Phosphate

The specimen of salt used was three times recrystallized. By precipitation of the phosphorus as magnesium pyrophosphate, the exact strength of the mother solution was ascertained.

Table XXII.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
16	164.3	68.4	215.3	68.2	268.5	67.3
32	182.4	75.9	238.7	75.6	298.9	74.9
128	212.1	88.3	278.4	88.2	350.9	87.9
512	231.6	96.4	304.7	96.5	384.6	96.4
1024	236.4	98.4	310.2	98.3	393.2	98.5
2048	240.3	100.0	315.6	100.0	399.0	100.0

Table XXIII.—Temperature Coefficients

V	35°–50° Cond. units	Per cent.	50°–65° Cond. units	Per cent.
16	3.40	2.07	3.55	1.65
32	3.75	2.06	4.02	1.69
28	4.42	2.08	4.83	1.73
512	4.87	2.10	5.33	1.75
1024	4.92	2.08	5.53	1.78
2048	5.02	2.09	5.56	1.76

Potassium Chlorate

The specimen used was recrystallized and dried in an air bath for two hours at 120°. The strength of the mother solution was obtained by weighing the pure and dry salt.

Table XXIV.—Conductivity

V	0°	12°.5	25°	35°
8	58.9	80.8	104.7	124.9
32	64.3	88.3	115.2	137.3
128	68.5	94.2	122.8	146.5
512	70.1	96.7	126.1	150:9
1024	70.6	97.7	127.8	153.1
2048	71.2	98.4	128.4	154.0
4096	72.4	100.7	131.4	157.6

Table XXV.—Temperature Coefficients

V	0°–12°.5 Cond. units	Per cent.	12°.5–25° Cond. units	Per cent.	25°–35° Cond. units	Per cent.
8	1.75	2.97	1.91	2.36	2.02	1.93
32	1.94	3.00	2.15	2.43	2.21	1.93
128	2.07	2.90	2.29	2.42	2.36	1.92
512	2.12	3.02	2.35	2.43	2.48	1.95
1024	2.15	3.04	2.42	2.47	2.52	1.97
2048	2.18	3.06	2.44	2.47	2.56	1.98
4096	2.25	3.09	2.46	2.44	2.62	1.98

Table XXVI.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	81.3	80.2	79.7	79.2
32	88.8	87.6	87.5	87.1
128	94.6	93.5	93.2	92.9
512	96.8	96.0	95.9	95.7
1024	97.5	97.2	97.2	97.1
2048	98.3	97.7	97.7	97.7
4096	100.0	100.0	100.0	100.0

Potassium Chlorate

The specimen of salt used for this series was the same as that used for the work at lower temperatures. It was purified and standardized in exactly the same way as above.

Table XXVII.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
8	125.4	78.3	158.6	77.6	192.1	76.8
32	137.3	85.8	173.4	84.9	211.9	84.8
128	146.4	91.4	185.0	90.6	228.8	91.6
512	151.2	94.4	193.4	94.6	239.1	95.7
1024	153.1	95.6	197.4	96.6	241.5	96.7
2048	158.1	98.7	200.8	98.2	244.9	98.0
4096	160.1	100.0	204.3	100.0	249.7	100.0

Table XXVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.22	1.77	2.23	1.40
32	2.41	1.76	2.57	1.48
128	2.57	1.76	2.92	1.57
512	2.81	1.85	3.05	1.57
1024	2.95	1.92	2.94	1.49
2048	2.85	1.80	2.94	1.46
4096	2.95	1.84	3.03	1.48

Potassium Perchlorate

This salt received two crystallizations. It was dried in the air bath for two hours at 130°.

Table XXIX.—Conductivity

V	0°	12°.5	25°	35°
32	65.1	89.8	116.9	139.6
128	68.9	95.0	125.1	149.5
512	71.7	98.2	129.0	154.2
1024	72.0	99.5	130.7	155.3
2048	73.3	101.2	132.6	158.6
4096	74.3	102.6	134.5	160.7

Table XXX.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	1.98	3.04	2.17	2.42	2.27	1.94
128	2.08	3.02	2.40	2.52	2.44	1.95
512	2.12	2.95	2.44	2.60	2.52	1.95
1024	2.20	3.05	2.49	2.50	2.56	1.95
2048	2.23	3.04	2.51	2.48	2.60	1.96
4096	2.26	3.04	2.55	2.49	2.62	1.94

Table XXXI.—Percentage Dissociation

V	0°	12°.5	25°	35°
32	87.6	87.6	86.9	86.9
128	92.7	92.5	93.0	93.0
512	96.5	95.7	95.9	95.3
1024	97.0	96.9	97.1	96.6
2048	98.6	98.5	98.5	98.6
4096	100.0	100.0	100.0	100.0

Potassium Perchlorate

The values given below were obtained from the same sample of salt as was used at lower temperatures. As before, it was recrystallized and dried in the air bath for two hours at 130°.

Table XXXII.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
32	139.8	85.8	178.0	86.2	217.2	86.4
128	150.3	92.3	190.2	92.1	232.7	92.6
512	153.9	94.5	194.3	94.1	237.7	94.6
1024	155.0	95.1	195.9	94.9	240.6	95.7
2048	157.5	96.7	200.0	96.9	244.2	97.2
4096	162.9	100.0	206.4	100.0	251.3	100.0

The conductivity values given by Ostwald for this salt are several units higher than those here recorded. Several of the above values were redetermined with a new specimen of pure potassium perchlorate, and very close agreements with the above values were obtained.

Table XXXIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	2.55	1.81	2.61	1.46
128	2.66	1.77	2.83	1.48
512	2.69	1.75	2.89	1.48
1024	2.73	1.76	2.98	1.52
2048	2.83	1.79	2.94	1.42
4096	2.90	1.78	2.99	1.44

Potassium Phosphate

The phosphorus content of the original solution was determined by means of magnesia mixture. Different specimens from Kahlbaum were used for the low and high temperature work.

Table XXXIV.—Conductivity

V	0°	12°.5	25°	35°
8	116.6	163.8	217.2	263.6
32	144.1	206.7	280.3	344.2
128	178.9	257.7	348.2	425.2
512	193.7	274.7	366.1	442.8
1024	192.1	271.5	362.5	440.1
2048	190.0	268.3	359.3	437.2
4096	179.0	252.0	336.7	407.6

Table XXXV.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	3.78	3.24	4.27	2.60	4.64	2.13
32	5.00	3.54	5.88	2.85	6.39	2.24
128	6.30	3.50	7.24	2.81	7.70	2.21
512	6.48	3.34	7.31	2.66	7.67	2.10
1024	6.35	3.30	7.28	2.68	7.76	2.14
2048	6.26	3.29	7.28	2.75	7.79	2.14
4096	5.84	3.27	6.78	2.69	7.09	2.10

Table XXXVI.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	60.2	59.6	59.3	59.5
32	74.4	75.2	76.5	77.7
128	92.9	93.8	95.1	96.0
512	100.0	100.0	100.0	100.0
1024	99.2	98.8	99.0	99.3
2048	98.0	97.3	98.1	98.7
4096	92.4	92.1	91.9	92.0

Potassium Phosphate

Table XXXVII.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
8	261.4	59.5	334.5	58.2	415.5	58.7
32	346.9	77.7	453.6	78.7	566.1	80.0
128	427.8	96.0	552.2	96.1	685.7	96.9
512	443.7	100.0	574.6	100.0	707.6	100.0
1024	439.8	99.3	565.1	98.3	697.3	98.5
2048	426.0	98.7	549.5	95.6	676.2	95.5
4096	402.5	92.0	517.1	90.0	646.9	91.4

Table XXXVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	4.73	1.79	5.40	1.61
32	7.29	2.04	7.50	1.65
128	8.46	1.99	8.90	1.61
512	8.78	1.98	8.87	1.54
1024	8.33	1.89	8.81	1.56
2048	7.49	1.71	8.45	1.53
4096	7.30	1.81	8.65	1.67

Calcium Chloride

The specimen of salt used was purified by two recrystallizations from conductivity water. The concentration of the mother solution was ascertained by weighing calcium as the oxide, CaO.

Table XXXIX.—Conductivity

V	0°	12°.5	25°	35°
2	80.5	109.6	142.1	169.1
8	95.3	132.1	172.5	207.4
32	106.4	149.3	197.5	238.0
128	117.8	165.6	219.2	265.8
512	124.0	174.8	232.4	281.9
1024	126.5	179.0	236.1	284.6
2048	131.4	185.0	245.0	298.3
4096	131.3	185.2	246.5	300.0

Table XL.—Temperature Coefficients

V	0°–12°.5 Cond. units	Per cent.	12°.5–25° Cond. units	Per cent.	25°–35° Cond. units	Per cent.
2	2.32	2.90	2.60	2.46	2.70	1.90
8	2.94	3.08	3.23	2.44	3.49	2.02
32	3.43	3.21	3.85	2.58	4.05	2.05
128	3.82	3.24	4.29	2.58	4.66	2.12
512	4.06	3.27	4.57	2.61	4.94	2.12
1024	4.20	3.39	4.70	2.68	4.85	2.05
2048	4.28	3.02	4.80	2.58	5.33	2.17
4096	4.31	3.26	4.90	2.59	5.35	2.17

Table XLI.—Percentage Dissociation

V	0°	12°.5	25°	35°
2	61.2	59.1	57.6	56.3
8	72.5	71.3	69.9	69.1
32	80.9	80.6	80.1	79.3
128	89.6	89.4	88.9	88.6
512	94.3	94.2	94.6	93.9
1024	96.2	96.1	95.7	94.8
2048	100.0	100.0	99.3	99.4
4096	99.9	99.9	100.0	100.0

Strontium Chloride

After the salt had been subjected to three recrystallizations the chlorine content in the mother solution was determined as silver chloride.

Table XLII.—Conductivity and Dissociation

V	35° μ_v	α	50° μ_v	α	65° μ_v	α
8	208.9	68.8	265.5	67.7	324.4	66.6
16	224.5	73.9	285.6	72.8	350.2	71.9
32	240.4	79.1	305.7	77.9	377.5	77.5
128	267.3	88.0	342.4	87.3	424.6	87.2
512	282.8	93.1	367.7	93.7	453.9	93.2
1024	286.8	94.4	373.0	95.1	463.3	95.2
2048	297.0	97.8	383.2	97.7	476.5	97.8
4096	303.7	100.0	392.2	100.0	486.9	100.0

Table XLIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	3.78	1.81	3.92	1.48
16	4.07	1.81	4.25	1.49
32	4.35	1.81	4.79	1.56
128	5.01	1.87	5.48	1.60
512	5.66	2.00	5.75	1.57
1024	5.75	2.01	6.02	1.62
2048	5.75	1.94	6.22	1.62
4096	5.90	1.94	6.32	1.61

Barium Bromide

After careful recrystallization of the salt, the exact barium content in the mother solution was determined as barium sulphate.

Table XLIV.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	222.0	70.5	280.1	69.2	340.1	68.4
16	237.8	75.6	301.1	74.4	367.6	73.9
32	251.8	80.0	320.2	79.1	392.8	79.0
128	278.4	88.5	358.0	88.5	439.2	88.3
512	295.1	93.8	379.6	93.8	467.6	94.0
1024	302.1	96.0	385.3	95.2	475.1	95.5
2048	305.5	97.1	393.9	97.4	484.6	97.4
4096	314.7	100.0	404.5	100.0	497.2	100.0

Table XLV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	3.87	1.74	4.00	1.42
16	4.22	1.77	4.43	1.47
32	4.56	1.81	4.84	1.51
128	5.31	1.91	5.41	1.51
512	5.63	1.91	5.87	1.54
1024	5.55	1.83	5.99	1.55
2048	5.90	1.93	6.05	1.54
4096	5.65	1.80	6.18	1.53

Barium Formate

The above salt was three times recrystallized. The concentration of the barium in the original solution was determined by weighing the barium as barium sulphate.

Table XLVI.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	158.8	66.1	201.0	64.2	245.4	63.6
16	178.4	74.3	227.3	72.6	275.1	71.4
32	196.6	81.9	252.1	80.5	307.3	79.7
128	225.4	93.8	289.6	92.4	359.6	93.3
512	237.8	99.0	308.2	98.4	383.6	99.5
1024	240.1	100.0	313.2	100.0	385.5	100.0
2048	239.8	99.9	309.5	98.8	376.4	97.6

Table XLVII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.81	1.77	2.96	1.47
16	3.26	1.83	3.19	1.43
32	3.70	1.88	3.68	1.46
128	4.28	1.89	4.67	1.61
512	4.69	1.97	5.03	1.63
1024	4.87	2.03	4.82	1.54
2048	4.65	1.94	4.46	1.44

Magnesium Chloride

The above salt was purified by three crystallizations. Precipitations of the magnesium as magnesium pyrophosphate determined the strength of the mother solution.

Table XLVIII.—Conductivity

V	0°	12°.5	25°	35°
4	80.2	112.1	147.3	177.6
8	87.6	123.2	162.1	196.1
32	100.0	141.1	187.1	226.4
128	110.2	156.1	208.0	252.4
512	115.7	164.3	219.4	266.8
1024	118.3	168.5	225.0	272.2
2048	120.2	172.8	230.2	280.0
4096	123.5	176.3	234.7	285.2

Table XLIX.—Temperature Coefficients

V	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.55	3.17	2.82	2.51	3.03	2.05
8	2.85	3.25	3.11	2.52	3.40	2.09
32	3.29	3.29	3.68	2.60	3.93	2.10
128	3.67	3.33	4.15	2.65	4.44	2.13
512	3.89	3.36	4.41	2.67	4.74	2.16
1024	4.02	3.39	4.52	2.68	4.72	2.09
2048	4.21	3.48	4.59	2.65	4.98	2.16
4096	4.22	3.32	4.67	2.64	5.05	2.15

Table L.—Percentage Dissociation

V	0°	12°.5	25°	35°
4	64.9	63.6	62.8	62.3
8	70.9	69.9	69.1	68.7
32	80.9	80.0	79.7	79.4
128	89.2	88.5	88.6	88.5
512	93.7	93.2	93.5	93.5
1024	95.8	95.6	95.8	95.4
2048	97.3	98.0	98.1	98.2
4096	100.0	100.0	100.0	100.0

Magnesium Sulphate

This salt was recrystallized three times. An attempt was made to get the purified and dried product anhydrous by heating it in an air bath for two hours at 225°. It was found that the anhydrous salt readily took up moisture from the air, and, furthermore, that the salt could not be obtained perfectly anhydrous at temperatures even higher than that stated above. Consequently, the mother solution was standardized by analysis, the sulphur being precipitated as barium sulphate.

Table LI.—Conductivity and Dissociation

V	35°		50°		65°	
	μ_v	α	μ_v	α	μ_v	α
2	72.4	27.6	90.5	26.5	106.5	25.2
8	104.0	39.6	131.0	38.3	155.4	36.8
16	120.4	45.8	150.7	44.1	179.0	42.4
32	139.0	52.9	174.6	51.1	208.6	49.4
128	180.7	68.8	230.3	67.4	279.1	66.0
512	224.7	85.6	288.1	84.3	353.1	83.6
1024	245.9	93.6	317.7	93.0	395.4	93.6
2048	262.6	100.0	341.7	100.0	422.6	100.0

Table LII.—Temperature Coefficients

V	35°–50° Cond. units	35°–50° Per cent.	50°–65° Cond. units	50°–65° Per cent.
2	1.21	1.67	1.07	1.18
8	1.80	1.73	1.63	1.24
16	2.02	1.68	1.89	1.27
32	2.37	1.71	2.27	1.30
128	3.31	1.83	3.25	1.41
512	4.23	1.88	4.32	1.50
1024	4.79	1.95	5.18	1.63
2048	5.27	2.01	5.39	1.58

Manganous Chloride

After the salt had been twice recrystallized from conductivity water, the manganese in the original solution was determined as the pyrophosphate.

Table LIII.—Conductivity and Dissociation

V	35° μv	35° α	50° μv	50° α	65° μv	65° α
2	142.5	49.3	177.3	47.5	210.5	44.9
8	191.5	66.3	242.3	64.9	293.7	62.7
16	210.3	72.8	266.8	71.5	326.6	69.7
32	226.5	78.4	289.1	77.5	357.0	76.2
128	252.9	87.6	325.0	87.2	402.3	85.9
512	274.7	95.1	356.2	95.5	447.4	95.5
1024	281.3	97.4	366.4	98.3	459.2	98.1
2048	288.8	100.0	372.9	100.0	468.4	100.0

Table LIV.—Temperature Coefficients

V	35°–50° Cond. units	35°–50° Per cent.	50°–65° Cond. units	50°–65° Per cent.
2	2.32	1.63	2.21	1.25
8	3.38	1.76	3.43	1.41
16	3.77	1.79	3.99	1.49
32	4.17	1.88	4.53	1.57
128	4.81	1.90	5.15	1.59
512	5.43	1.97	6.08	1.71
1024	5.67	2.01	6.19	1.79
2048	5.61	1.94	6.37	1.71

Manganous Nitrate

This salt was once recrystallized, care being taken to prevent decomposition. The manganese was determined as manganese pyrophosphate.

Table LV.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
2	139.6	52.0	171.5	49.3	205.0	47.5
8	183.8	68.5	231.7	67.0	279.9	64.8
32	216.8	80.8	277.0	80.0	338.8	78.5
128	242.0	90.2	310.5	89.7	382.8	88.7
512	256.5	95.8	335.0	96.8	413.5	95.8
1024	264.7	98.7	341.3	98.6	425.4	98.6
2048	268.3	100.0	346.3	100.0	431.5	100.0

Table LVI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.13	1.53	2.23	1.30
8	3.19	1.73	3.21	1.39
32	4.01	1.85	4.12	1.49
128	4.57	1.89	4.82	1.55
512	5.20	2.02	5.23	1.56
1024	5.11	1.93	5.61	1.64
2048	5.20	1.94	5.68	1.64

Aluminium Chloride

The specimen of salt used was not recrystallized. It was, however, tested for sulphates and nitrates with negative results. The test for iron disclosed a mere trace of that element. It was only by using a fairly large amount of the substance that a positive result was obtained.

Table LVII.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
4	231.6	45.8	296.9	42.2	361.4	37.9
8	266.8	52.8	341.6	48.6	419.1	44.0
16	291.6	58.6	381.1	54.2	470.9	49.4
64	350.3	69.3	455.5	64.8	567.3	59.5
512	429.3	85.0	567.5	80.7	730.0	76.6
1024	449.8	89.1	609.3	86.6	796.7	83.6
2048	479.9	95.0	647.5	92.1	868.5	91.1
4096	505.1	100.0	703.2	100.0	953.2	100.0

Table LVIII.—Temperature Coefficients

V	35°–50° Cond. units	35°–50° Per cent.	50°–65° Cond. units	50°–65° Per cent.
4	4.35	1.88	4.30	1.45
8	4.99	1.87	5.16	1.51
16	5.66	1.91	5.99	1.58
64	7.02	2.00	7.45	1.62
512	9.22	2.15	10.83	1.91
1024	10.63	2.36	12.49	2.05
2048	11.17	2.33	14.73	2.27
4096	13.21	2.62	16.66	2.37

Aluminium Nitrate

The salt used was a fine specimen obtained from Kahlbaum. Recrystallization was effected by desiccation over sulphuric acid. The powdered salt was then allowed to stand in a vacuum over potassium hydroxide for several days. The aluminium in the mother solution was determined as aluminium oxide.

Table LIX.—Conductivity and Dissociation

V	35° μ_v	35° α	50° μ_v	50° α	65° μ_v	65° α
4	219.0	45.7	276.0	42.0	338.6	37.3
8	252.0	52.6	320.8	48.8	393.9	43.4
32	306.3	64.0	394.3	60.0	487.3	53.6
128	358.0	74.7	464.4	70.7	583.9	64.3
512	407.2	85.0	535.8	82.0	685.9	75.5
1024	433.9	90.6	575.8	87.7	750.5	82.6
2048	457.4	95.5	613.3	93.4	820.9	90.4
4096	478.9	100.0	656.6	100.0	908.2	100.0

Table LX.—Temperature Coefficients

V	35°–50° Cond. units	35°–50° Per cent.	50°–65° Cond. units	50°–65° Per cent.
4	3.80	1.73	4.17	1.51
8	4.57	1.81	4.87	1.52
32	5.87	1.92	6.20	1.57
128	7.10	1.98	7.97	1.72
512	8.84	2.14	10.07	1.88
1024	9.46	2.18	11.65	2.01
2048	10.40	2.27	13.84	2.25
4096	11.86	2.47	16.77	2.55

Aluminium Sulphate

The above salt was recrystallized by slowly desiccating a saturated solution over sulphuric acid. The exact strength of the mother solution was ascertained by determining the sulphur as barium sulphate.

Table LXI.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
4	114.2	16.5	136.5	14.6	152.8	12.5
8	141.3	20.4	166.7	17.8	185.7	15.2
32	198.9	28.7	236.7	25.3	266.2	21.8
128	278.3	40.1	339.9	36.3	395.1	32.4
512	395.5	57.0	497.3	53.1	594.6	48.7
1024	478.2	68.9	613.2	65.5	740.2	60.6
2048	571.7	82.4	746.8	79.8	943.0	72.2
4096	693.5	100.0	936.1	100.0	1221.2	100.0

Table LXII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	1.49	1.22	1.09	0.8
8	1.69	1.20	1.27	0.76
32	2.52	1.27	1.97	0.83
128	4.11	1.48	3.67	1.08
512	6.79	1.72	6.49	1.31
1024	9.00	1.88	8.47	1.38
2048	11.67	2.04	13.08	1.75
4096	16.17	2.33	19.01	2.03

Chromic Chloride (Violet Variety)

The sample of the above salt was secured from Kahlbaum, and it was purified by recrystallization from conductivity water. This was effected by the slow desiccation of a saturated solution over sulphuric acid. The powdered salt was afterwards dried over potassium hydroxide in a vacuum desiccator for a period of about a week. A gravimetric determination of the chromium as chromic oxide gave the exact strength of the original solution.

Table LXIII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	256.7	41.0	332.3	39.7	410.0	37.2
32	330.5	52.7	431.2	51.6	538.5	48.9
128	406.0	64.8	534.3	63.9	681.5	61.9
512	486.5	77.6	650.9	77.9	834.4	75.7
1024	543.7	86.7	724.2	86.6	941.3	85.5
2048	582.8	93.0	783.9	93.8	1015.7	92.2
4096	626.7	100.0	836.5	100.0	1101.4	100.0

Table LXIV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	5.04	1.96	5.18	1.56
32	6.71	2.03	7.15	1.66
128	8.55	2.11	9.81	1.83
512	10.96	2.25	12.23	1.87
1024	12.03	2.21	14.47	1.99
2048	13.42	2.30	15.45	1.53
4096	13.99	2.23	17.66	1.60

Chromic Nitrate (Violet Variety)

This salt was recrystallized by allowing a concentrated solution to desiccate over phosphorus pentoxide. The chromium content of the mother solution was determined as chromic oxide.

Table LXV.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	180.4	32.1	231.8	30.2	278.5	27.9
8	260.3	46.4	335.9	43.8	416.3	41.7
16	292.5	52.1	380.6	49.6	473.8	47.4
32	322.1	57.4	420.5	54.8	531.2	53.2
128	388.2	69.1	511.2	66.6	658.9	65.9
512	472.2	84.1	634.7	82.7	821.2	82.2
1024	514.7	91.7	692.0	90.2	894.4	89.5
2048	561.5	100.0	767.0	100.0	999.0	100.0

Table LXVI.—Temperature Coefficients

V	35°–50° Cond. units	Per cent.	50°–65° Cond. units	Per cent.
2	3.43	1.90	3.11	1.34
8	5.04	1.93	5.36	1.59
16	5.87	2.01	6.22	1.63
32	6.76	2.09	7.38	1.75
128	8.20	2.11	9.85	1.92
512	10.83	2.29	12.43	1.96
1024	11.82	2.32	13.49	1.95
2048	13.70	2.44	15.47	2.01

Chromic Sulphate (Violet Variety)

This salt was recrystallized by slow desiccation of a concentrated solution over sulphuric acid. The powdered salt was afterwards dried in a vacuum over potassium hydroxide. The chromium in the original solution was determined as chromic oxide. The conductivity values obtained not agreeing with those of other investigators, it was deemed advisable to redetermine the chromium in the mother solution. This was done and a very good agreement with the results of the previous analysis was obtained.

Table LXVII.—Conductivity and Dissociation

V	35° μv	α	50° μv	α	65° μv	α
8	110.4	19.3	128.1	14.5	139.9	12.4
32	179.0	31.3	209.7	23.8	228.5	20.2
128	265.5	46.5	328.0	37.2	370.6	32.7
512	362.2	63.4	488.8	55.5	585.3	51.7
1024	418.9	73.3	585.4	66.5	732.1	64.6
2048	458.8	80.3	713.3	80.9	905.2	80.0
4096	571.2	100.0	880.9	100.0	1132.4	100.0

Table LXVIII.—Temperature Coefficients

V	35°–50° Cond. units	Per cent.	50°–65° Cond. units	Per cent.
8	1.18	1.07	0.79	0.62
32	2.05	1.14	1.25	0.60
128	4.17	1.57	2.84	0.86
512	8.44	2.33	6.43	1.32
1024	11.10	2.65	9.78	1.67
2048	16.97	3.69	12.79	1.78
4096	20.65	3.61	16.77	1.94

Lead Nitrate

The specimen of salt used was twice recrystallized. The purified product was dried to constant weight in the air bath at about 120°. A weighed amount of salt gave the exact concentration of the mother solution.

Table LXIX.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	111.5	36.0	143.0	35.9	175.9	35.8
8	170.2	54.9	218.4	54.8	267.8	54.5
16	196.6	63.5	251.7	63.2	309.4	62.9
32	220.4	71.2	281.6	70.8	347.8	70.7
128	261.0	84.3	333.3	83.8	410.2	83.4
512	291.0	93.9	369.6	92.9	455.0	92.5
1024	300.0	96.9	385.1	96.8	477.7	97.2
2048	309.6	100.0	397.9	100.0	491.8	100.0

Table LXX.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.10	1.88	2.19	1.53
8	3.21	1.88	3.29	1.51
16	3.74	1.93	3.85	1.53
32	4.08	1.81	4.41	1.53
128	4.83	1.85	5.13	1.53
512	5.24	1.80	5.69	1.54
1024	5.67	1.89	6.17	1.60
2048	5.89	1.90	6.36	1.64

Nickel Nitrate

This salt was purified by three recrystallizations. The nickel content of the mother solution was ascertained by driving off the oxides of nitrogen and reducing the nickel oxide to constant weight in a stream of hydrogen.

Table LXXI.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	145.5	50.9	182.7	49.4	219.7	48.4
8	188.8	66.0	239.5	64.8	291.9	64.3
32	218.4	76.4	278.3	75.3	342.7	75.7
128	243.6	85.2	310.6	84.0	386.1	85.0
512	262.0	91.7	336.2	91.0	416.0	91.6
1024	267.6	93.6	344.6	93.2	427.3	94.1
2048	285.8	100.0	369.8	100.0	453.9	100.0
4096	281.2	98.4	364.1	98.5	449.8	99.1

Table LXXII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.48	1.70	2.47	1.35
8	3.38	1.78	3.49	1.42
32	3.99	1.82	4.29	1.54
128	4.47	1.83	5.03	1.65
512	4.95	1.88	5.32	1.58
1024	5.13	1.92	5.53	1.60
2048	5.60	1.96	5.61	1.52
4096	5.53	1.97	5.72	1.57

Copper Ammonium Sulphate

After one recrystallization the sulphuric acid content in the above salt was accurately determined by means of barium chloride.

Table LXXIII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
4	225.2	36.9	278.3	35.3	334.7	35.6
8	260.0	42.7	323.5	41.0	383.1	39.2
32	333.6	54.7	417.5	53.0	496.9	50.9
128	416.9	68.4	521.1	66.1	630.1	64.5
512	499.7	82.0	634.0	80.4	768.9	78.7
1024	546.8	89.7	697.8	88.5	850.8	87.1
2048	578.3	94.9	744.1	94.4	916.2	93.8
4096	609.5	100.0	788.3	100.0	976.8	100.0

Table LXXIV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	3.54	1.57	3.76	1.35
8	4.23	1.63	3.97	1.23
32	5.59	1.67	5.29	1.26
128	6.96	1.66	7.27	1.39
512	8.95	1.79	8.99	1.42
1024	10.67	1.95	10.20	1.46
2048	11.05	1.94	11.47	1.54
4096	11.92	1.95	12.57	1.59

Uranyl Sulphate

As there was only a small quantity of this salt available, it was not purified. After several days' drying in a vacuum over

potassium hydroxide, the uranium in the mother solution was determined as the oxide, U_3O_8.

Table LXXV.—Conductivity and Dissociation

	35°		50°		65°	
V	μv	α	μv	α	μv	α
8	153.0	33.2	172.5	30.2	189.9	28.4
32	192.3	41.7	215.3	37.7	231.0	34.6
128	248.6	53.9	279.5	49.0	300.1	44.9
512	322.1	69.8	369.5	64.7	403.7	60.4
1024	360.9	78.2	421.7	73.9	471.0	70.5
2048	413.5	89.6	498.9	87.4	562.6	84.2
4096	461.4	100.0	570.7	100.0	667.9	100.0

Table LXXVI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.30	0.85	1.16	0.67
32	1.53	0.79	1.05	0.49
128	2.06	0.83	1.37	0.49
512	3.16	0.98	2.28	0.62
1024	4.05	1.12	3.29	0.78
2048	5.69	1.13	4.25	0.85
4096	7.29	1.23	6.48	1.14

SPECIAL WORK

The conductivity data for chromium salts, as is also the case with other salts which are strongly hydrated and hydrolyzed, are so discordant that it was decided to do some special work on such salts. It was hoped to arrive at a possible explanation for the discordant results obtained by different investigators.

Insolubility of Jena Glass

The vessels which held the solutions used in this work were of Jena glass. As far as the solvent action of water on the glass is concerned, it is evident that by treating them in the following way all soluble matter can be removed from them up to temperatures as high as 90°. A chromic acid cleaning mixture had stood in the vessels all summer. After rinsing, they were filled with distilled water, tightly corked, and warmed to 90° for eight hours. Two of the bottles were

carefully rinsed and filled with pure water whose conductivity was known. The stoppers were tightly wired into place, and the two bottles containing the water were warmed to 90° for four hours. They were allowed to stand for two days at room temperature, and then the conductivities of the two specimens of water were determined. The results are seen best when expressed as follows: R is the resistance in the rheostat and A the reading on the bridge.

Reading for unheated water at 25°

$$R = 2000, A = 515$$

Readings at 25° for the water which had been heated in bottles to 90° for four hours

$$(1)\ R = 3000, A = 520$$
$$(2)\ R = 2000, A = 517$$

From these results and others carried out in an analogous manner, it was concluded that practically all soluble matter had been removed from our vessels.

A Dehydrolytic Time Factor in the Case of Chromic Salts

The study of the green and violet varieties of chromic salts has long been a favorite subject of investigation. The conductivity method[1] shows that the violet variety has a smaller conductivity than the corresponding concentration of the green variety, and that with increase in dilution, the conductivity of the violet salt increases at a greater rate than that of the green. To explain the greater conductivity of the green modification, several theories have been advanced. The one generally accepted to-day, and substantiated by the work of Recoura,[2] Whitney,[3] Denham,[4] Graham,[5] and others, is that the green variety contains some of the violet variety plus the products of its hydrolysis—a complex chromium salt and the corresponding acid. If this is true, the law of mass action would explain why the conductivity of the violet variety increases more rapidly with dilution than the green variety.

[1] Carnegie Institution of Washington, Publication No. **170**, p. 35.
[2] Ann. chim. phys., [7] **4**, 494 (1895).
[3] Z. physik. Chem., **20**, 40 (1896).
[4] Z. anorg. Chem., **57**, 361 (1908).
[5] This Journal, **48**, 145 (1912).

For those salts which are hydrolyzed by rise in temperature, it was seen that unless the products of hydrolysis recombine as the temperature is lowered our method for the purification of salts for conductivity measurements must be changed. This point was tested out for the chromic salts.

A specimen of violet chromic chloride secured from Kahlbaum was recrystallized by allowing a solution saturated at room temperature to desiccate over phosphorus pentoxide. The chromium content of the mother solution was determined as the oxide Cr_2O_3. From the mother solution, N/32 and N/512 solutions were prepared. Four of the bottles, treated as above described to remove soluble matter, were filled with the N/32 chromic chloride solution. The stoppers of three of them were tightly wired into place. The first was warmed to 50° for two hours, the second to 65° for two hours, the third to 90° for two hours. The fourth was not heated. The heated solutions were quickly cooled to room temperature, and their conductivities determined at 35°, 50° and 65°, along with the solution which had not been heated. The following results were obtained:

V	t	Not heated	Heated to 50°	Heated to 65°	Heated to 90°
32	35°	330.5	331.4	342.0	415.9
32	50°	424.6	429.7	439.0	519.0
32	65°	532.4	536.9	544.6	624.2

The same process was repeated with the N/512 chromium chloride solution.

V	t	Not heated	Heated to 50°	Heated to 65°	Heated to 90°
512	35°	487.4	489.5	500.6	559.7
512	50°	652.2	656.7	667.7	724.6
512	65°	842.5	843.8	856.6	915.1

The results for the more dilute solutions are of the same character as those for the more concentrated. They indicate that the hydrolysis of chromium salts increases rapidly with rise in temperature. Its effect is very marked even in the N/32 solution. If we subtract the conductivities of the solutions which were not heated from the conductivities of the solutions

which were heated to 90°, we note that the effect of hydrolysis, considering the amount of salt present in the two solutions, is very much more marked in the case of the more dilute solution.

$N/32\ CrCl_3$		$N/512\ CrCl_3$	
35°	85.4	35°	72.3
50°	94.4	50°	72.4
65°	91.8	65°	72.6

Furthermore, it is evident that the increase in hydrolysis, at least for the N/512 solution of chromic chloride, is fairly constant, regardless of the temperature at which the conductivity readings were taken. This points to the conclusion that dehydrolysis did not take place to any appreciable extent as the solution was cooled down, and that as the temperature was again raised the conductivity of the green variety increased at about the same rate as the conductivity of the violet variety.

The following experiment was carried out to throw some light on the length of time required for the products of hydrolysis to recombine:

The N/512 solution of chromic chloride which had been heated to 90° for two hours was allowed to stand at room temperature for twenty days, and its conductivity again determined at 35°. The value found was 508, while the value found shortly after heating was 559.7. The unheated solution gave a conductivity of 487.4. A similar experiment with N/512 chromic chloride was carried out. The solution had been heated to 90° for two hours, and allowed to stand at room temperature for twenty days. Its conductivity was determined at 65°, and the value 885 was found. The conductivity shortly after heating was 915.1. That of the unheated solution was 842.5. Here we evidently have a dehydrolytic time factor which persists for days and perhaps months. From these results it is concluded that, in the purification of chromic salts, great care must be taken to keep the temperature of the solution lower than the lowest temperature at which conductivity readings are to be made. The discordant values obtained by previous investigators are perhaps due to their

method of purification and failure to take into account the dehydrolytic time factor.

Evidently, it is a matter of great importance for conductivity methods to determine whether other salts which are easily hydrolyzed show a similar phenomenon. The method by which a salt is ordinarily purified is to cool quickly a solution which is saturated at a certain high temperature. In warming solutions of such salts, it is conceivable from the previous work that, upon crystallization, they might take out of solution an excess of one of the products of hydrolysis, if the acid and base did not immediately recombine as the solution was cooled. In view of the fact that it is just such kinds of salts that have been giving trouble in conductivity measurements, it seemed desirable to carry out the following experiments:

A specimen of aluminium sulphate from Kahlbaum was recrystallized by allowing a solution saturated at room temperature to desiccate over phosphorus pentoxide. The sulphuric acid in the original solution was determined as barium sulphate. Two bottles were filled with a N/32 solution, and two more with a N/512 solution. One bottle containing the N/32 solution and another containing the N/512 solution were securely stoppered, and both warmed to 85° for two hours. These solutions were quickly cooled to room temperature and their conductivities determined as soon as possible at 35°.

Aluminium Sulphate

V	t	Not heated	Heated to 85°
32	35°	205.8	206.4
512	35°	413.6	417.0

A similar experiment was carried out with magnesium chloride. The salt was purified by recrystallization from water, and the magnesium in the mother solution weighed as magnesium pyrophosphate. Two bottles, one containing the N/32 solution, the other containing the N/512 solution, were heated to 85° for $^1/_2$ hour. Both were tightly stoppered. They were quickly cooled to room temperature, and their conductivities determined at 25°.5, along with two other solutions which had not been heated.

Magnesium Chloride

V	t	Not heated	Heated to 85°
32	25.5	187.6	188.7
512	25.5	222.7	222.5

Other salts were worked with, and results of the same general character were obtained. These results point to the conclusion that it is usually safe to heat a salt during its purification almost up to the temperature at which it will decompose without influencing the conductivity readings. The only exception to this rule which was encountered applies to the chromic salts existing in two modifications. Of course, the hydrolysis of these salts is somewhat different from that of the ordinary salts.

The Water Correction as Influenced by Various Conditions

The conductivity of the water used in making up the solutions, when multiplied by the number expressing the volume of the solution, gives the water correction which must be subtracted from the molecular conductivity of the solution to obtain the true molecular conductivity of the salt in question. It is evident that any condition influencing the conductivity of the water will have an appreciable effect when multiplied by such numbers as 2048 and 4096. It is at these dilutions that the salt is assumed to be completely dissociated, and, consequently, an erroneous water correction would vitiate the μ_∞ values for the salt, and therefore its percentage dissociation. In the following experiments, several factors influencing the water correction were taken into account.

A. The water cell filled with conductivity water flowing at a rapid rate during a time when the air conditions in the room were much better than the normal conditions. The conductivity of the water was determined at 35° and the correction factors worked out for dilutions of N/1024, N/2048 and N/4096.

V	Correction
1024	1.74
2048	3.47
4096	6.95

B. Conductivity water was allowed to flow into a clean beaker at a rapid rate. The water was then exposed to the air for about three minutes at a time when the air conditions in the room were about normal. The time of exposure is somewhat less than the time required for making up a dilute solution and transferring it to the cell. The correction factors at 35° in this case were:

V	
1024	1.78
2048	3.56
4096	7.12

C. For this experiment, the air in the room was made less pure than normal. Three Bunsen burners were lighted for fifteen minutes, also a bottle containing ammonium hydroxide and another containing hydrochloric acid had been uncorked for an instant. The water was allowed to drop into the water cell so that a large surface of the water would be exposed to the air. The cell, holding about 60 cc., was filled during the course of two minutes. On the average a burette is hardly drained during that time. The correction factors at 35° were:

V	
1024	2.34
2048	4.68
4096	9.35

This work was repeated and results of a very similar character were obtained.

It is evident from the above work that errors larger than a per cent. may be introduced into conductivity work unless the proper water corrections are applied. The purity of the air in the room, during the times at which solutions are made up and the water cell filled, should be about the same. Furthermore, to obtain comparable results, the filling of the water cell should be so carried out that the water is exposed to the air for about the same period of time, and under the same conditions, as the more dilute solutions. These factors are more important for accurate conductivity work than has hitherto been realized. If the air conditions in the room were

good at the time the water cell was filled, and bad at the time the solutions were made up, the μ_∞ values would be too large, and too small when the reverse conditions exist. In this laboratory care is taken to have the air conditions always about the same, and the air as free from impurities as possible.

Dissociation as Measured by the Kohlrausch Conductivity Method

It is generally believed that the dissociation values, as obtained by the conductivity method, for salts which are not hydrated and hydrolyzed are correct to within the limits of experimental error. Of course, if a strongly concentrated solution of such a salt was used, the effect of viscosity would interfere with the velocities of the ions, and, consequently, the observed dissociation. It has been noted in this work that a great majority of the salts worked with did not reach complete dissociation even at a dilution of $V = 4096$. An attempt to work at dilutions beyond this proved to be impractical. Large experimental errors are involved in working with such small quantities of substance, and the effect of the air conditions on the water correction is very great.

It was noted, from the dissociation values obtained in this work, that the percentage difference between the μ_∞ value and the molecular conductivity of the next more dilute solution, as a rule, showed an increase with rise in temperature.

To throw more light upon the correctness of the above observation, some carefully prepared solutions of salts but little hydrolyzed and hydrated in dilute solutions were used. They were pure sodium chloride and pure sodium perchlorate. Special care was taken, as has already been explained, to apply the proper water correction.

For sodium chloride the following results were noted:

V	0°	12°.5	25°	35°
512	62.3	...	...	...
1024	63.2	88.6	116.9	142.6
2048	63.4	89.5	118.4	143.8
4096	63.6	90.2	120.0	145.5

The results for sodium perchlorate are very similar. They have already been tabulated (Table XVII).

It is evident that, as the temperature rises, the percentage increase in conductivity obtained by subtracting from the μ_∞ value the molecular conductivity of the next more dilute solution slowly becomes greater. We have reached with certainty the μ_∞ value only at 0°. For higher temperatures, it is necessary to work at greater dilutions to obtain the true μ_∞ value, and this, as we have seen, is impractical.

What is here brought out on a small scale becomes much more pronounced for salts which are strongly hydrated and hydrolyzed. The chromium and aluminium compounds illustrate this point very well (see Tables LXII to LXIX, inclusive).

If the salt does not reach a decided μ_∞ value at 0° for a dilution $V = 4096$, it is less probable that it will at any higher temperature, if for no other reason than because with rise in temperature the association of the solvent and its dielectric constant become less, and consequently its dissociating power is less. If the salt is strongly hydrolyzed or polymerized, the further removed from the true μ_∞ value will be the μ_v value obtained at a dilution $V = 4096$. Generally, in the dilute solutions, rise in temperature very greatly increases the effect of any one of these factors, and causes the true μ_∞ value to become more and more removed from the μ_v value obtained at a dilution $V = 4096$.

Hydrolysis is probably the chief factor in making it appear that a salt is not completely dissociated in our very dilute solutions. Aqueous solutions of many salts show an acid or basic reaction at ordinary temperatures. If we consider the case of ammonium chloride dissociated into ammonia and hydrochloric acid gas at high temperatures, we perhaps have a picture of how a strong acid and strong base in aqueous solution may exist in equilibrium with the salt molecules and water at high temperatures. As is well known, the effect of dilution and rise in temperature is to increase the hydrolysis. Consequently, at high temperatures to reach that point where there is no further increase in conductivity, it would be necessary to work with exceedingly dilute solutions. A large number of salts are but little hydrolyzed or polymerized in dilute solutions, and in such cases we can reach μ_∞ values

which are close to the correct ones. The presence of hydrated ions would necessarily make the observed dissociation too low. It does not seem probable that conductivity methods will, in the near future, be modified so that we can measure accurately the dissociation of salts strongly hydrated, hydrolyzed or polymerized. As a means of studying solutions, and obtaining the dissociation of electrolytes neither strongly hydrated, hydrolyzed nor polymerized, the conductivity method has been and probably will continue to be of great service.

DISCUSSION OF THE CONDUCTIVITY TABLES

Conductivities

Several of the salts studied in this investigation showed conductivities that are very interesting. Perhaps most interesting of all is that of ammonium acid sulphate. It is a ternary salt showing small dissociation in concentrated solutions. Its exceptionally high conductivity is probably due to the presence of the hydrogen ion. Because of small hydration, hydrolysis and depolymerization in concentrated solutions its conductivity is little increased by rise in temperature. At a dilution $V = 32$, hydrolysis and depolymerization evidently become very marked, and from then on its conductivity increases rapidly with rise in temperature and increase in dilution.

The high conductivity of potassium phosphate cannot fail to attract attention. It is a quaternary electrolyte strongly dissociated in concentrated solutions. Evidently, its complex ions break down in concentrated solutions, causing considerable hydrolysis. At the dilution $V = 512$ there is no further increase in conductivity with rise in temperature and increase in dilution. This is the only salt studied that gave clean cut μ_∞ values. It should be noted that it crystallizes without water, and, therefore, is but little hydrated in solution, and that the breaking down of its complex ions, giving rise to hydrolysis, produces its maximum effect in fairly concentrated solutions.

The conductivities of the aluminium and chromium compounds are very high and strikingly similar. The presence of a large number of ions, hydration and hydrolysis, condition

the large conductivity of these salts. The conductivity of aluminium sulphate in concentrated solutions is much less than that of either the nitrate or chloride. The same applies to the chromium salt, as does also the following. In dilute solutions, probably due to depolymerization and hydrolysis, the conductivity of the sulphates is much greater than that of the chlorides or nitrates.

Due to the greater weight of the anion and the smaller degree of dissociation, the conductivity of sodium chlorate is less than that of sodium chloride. That of sodium perchlorate is slightly greater than the conductivity of sodium chlorate, because of its greater dissociation. The conductivities of sodium chlorate and sodium perchlorate are less than the conductivities of potassium chlorate and potassium perchlorate. Since the dissociations of the sodium salts are greater than those of the potassium salts, and the potassium cation has a larger mass and atomic volume than the sodium cation, it would be a difficult matter to explain the above fact without the solvate theory. The sodium ion is more hydrated in solution than the potassium ion, and must draw with it, through the solvent, a more complex hydrate, which necessarily decreases its velocity. It should be noted that sodium perchlorate crystallizes with one molecule of water.

Potassium perchlorate is dissociated to a greater extent than potassium chlorate, except at 0°. Its conductivity is at all temperatures higher than that of potassium chlorate for the corresponding dilutions.

Dissociations

With the single exception of potassium phosphate, dissociation decreases with rise in temperature, as we should expect from the Thomson-Nernst hypothesis and the relation pointed out by Dutoit and Aston. In the case of potassium phosphate, there is a marked increase in dissociation with rise in temperature except for the most concentrated solution. Contrary to the usual course of events, ionic complexes appear to be more rapidly broken down at a low temperature than at a high one. As the complex breaks down hydrolysis takes

place. It may be found that the increase is due to an abnormal exothermic heat of dissociation of this salt. It is evident from the results that the conductivity of the N/32 solution at 0° increases more rapidly with dilution than at any higher temperature.

The dissociations of salts of metals in the same group having a similar chemical composition are of the same order of magnitude. As a general rule, the sulphates in concentrated solutions are less dissociated than the corresponding nitrates and chlorides. This is probably due to the polymerization of the sulphates. Salts of metals in the second group are dissociated considerably less than salts of the alkali metals, under the same conditions of temperature and dilution. As a rule, the dissociation of any chloride, nitrate, sulphate, etc., decreases as the valence of its cation increases.

According to conductivity measurements, it is only the salts that are strongly hydrolyzed and hydrated that show any marked decrease in dissociation with rise in temperature. The sulphates of chromium and aluminium show a very marked decrease. It is probably due to the fact that with rise in temperature and dilution the polymers are rapidly broken down. If it were possible to measure the true μ_∞ value of these salts, the decrease in dissociation with rise in temperature, as measured by the conductivity method, would be much greater than that indicated by the tabulated results.

Temperature Coefficients

Temperature coefficients in conductivity units, as Jones and his coworkers have often pointed out, were found to increase with rise in temperature and increase in dilution. Ammonium acid sulphate presents a remarkable exception to this rule. Its coefficients not only decrease, but for a solution of a concentration $V = 512$ or less, and the temperature range 35°–65°, its coefficients are negative. In concentrated solutions and over the temperature range 35°–65°, chromium, aluminium and uranyl sulphates also showed decreasing temperature coefficients. Why the conductivity of the salt should begin to increase less

rapidly at these high temperatures than it does at a lower temperature is unknown.

Ammonium acid sulphate, for the concentrated solutions, shows but a very small increase in conductivity with rise in temperature. Its increase is greatest the lower the temperature range. If the conductivity of its 0.5 N solution increased with rise in temperature at the same rate as that for chromic nitrate, we would have at 65° a conductivity of over 600 instead of 235.5. The small increase in conductivity of the concentrated solutions indicates small hydrolysis and hydration. The depolymerization of the molecules must also be small. With increase in dilution some one of these factors, or, possibly, all of them act so as to increase greatly the conductivity with rise in temperature. In these dilutions temperature coefficients approaching more nearly to the normal coefficients are obtained. This points to the conclusion that the presence of a large number of unionized molecules are more capable of holding in check, with rise in temperature, the factors that ordinarily cause conductivity to increase with rise in temperature. The nature of sulphates in aqueous solution is not well understood, and merits closer and more elaborate study.

Large temperature coefficients are for the most part conditioned by hydration and hydrolysis. There two factors are evidently closely connected. It may be that water of hydration is more readily dissociated than water which is not in combination with the dissolved particles. The salts that are most strongly hydrated are, as a rule, the ones that are strongly hydrolyzed and most soluble. Jones and his coworkers[1] have already pointed out a number of relations existing between temperature coefficients of conductivity and the solvate theory of solution. The relations which they have discovered are confirmed by this work.

The remarkable increase in the temperature coefficients of conductivity of chromium and aluminium sulphates with rise in temperature and increase in dilution must attract attention. They finally reach values greater than those of any other salt

[1] Carnegie Institution of Washington, Publication No. **60**, pp. 77–83.

studied. In dilute solutions, rapid depolymerization probably takes place with rise in temperature. The complex hydrates are readily broken down and hydrolysis increases. In concentrated solutions the effect of these factors with rise in temperature is very small.

Not much of interest can be deduced from the temperature coefficients in per cent. Jones[1] has pointed out that where $V = 8$ and the temperature range 25°–35°, the average value of the coefficient for a large number of widely different compounds is close to 2. Without an exception the temperature coefficients of conductivity in per cent. decrease with rise in temperature. Here, again, the coefficients of the sulphates are abnormal. Ammonium acid sulphate, chromic sulphate, uranyl sulphate and aluminium sulphate show negative coefficients in concentrated solutions. Those of chromium, aluminium and uranyl sulphates pass through a minimum. Ordinarily, a salt strongly hydrated and hydrolyzed shows a decided increase in the percentage temperature coefficients with increase in dilution. Those for salts not hydrated, hydrolyzed or polymerized are fairly constant.

SUMMARY

1. Some of the more important relations earlier pointed out by Jones and his coworkers, which the results obtained in this work confirm, are as follows:

Conductivity increases with temperature and dilution.

As a rule, temperature coefficients in conductivity units increase with rise in temperature. Salts strongly hydrated have large coefficients, those not strongly hydrated have small coefficients. The temperature coefficients are of the same order of magnitude for salts having approximately the same hydrating power. They increase with dilution, and the increase is greatest for those substances with large hydrating power.

With but one exception dissociation was found to decrease with rise in temperature.

Temperature coefficients in per cent. decrease with rise in temperature.

[1] Carnegie Institution of Washington, Publication No. **170**, pp. 77–83.

2. Abnormal and striking relations appearing in many of the conductivity tables have been pointed out, and in most cases satisfactory explanations, based upon what we to-day know in regard to the nature of solution, could be offered.

3. A dehydrolytic time factor in the case of chromic salts was observed. It was pointed out that in purifying a chromic salt for conductivity work, it must not be heated to a temperature higher than that at which its conductivity is to be taken, since the dehydrolysis time factor persists for months.

4. Other salts readily hydrolyzed were tested for dehydrolytic time factors. It was concluded that in purifying such salts it is safe to heat their solutions up to temperatures not far from the temperature at which they would decompose.

5. The effect of the air conditions on the water correction was brought out in a quantitative way, and other suggestions made to improve the accuracy of conductivity measurements.

6. The influence of hydration, hydrolysis and polymerization on conductivity measurements has been discussed, and it is concluded that the Kohlrausch conductivity method is not a good one for measuring the dissociation of sulphates which are strongly polymerized, nor for measuring the dissociation of any electrolyte which is at the same time hydrated and hydrolyzed.

Chemical Laboratory
Johns Hopkins University
January, 1913

REVIEWS

Soil Conditions and Plant Growth. By Edward J. Russell, D.Sc. (Lond.), Goldsmiths' Company's Soil Chemist, Rothamsted Experimental Station, Harpenden. With diagrams. Monographs on Biochemistry, edited by R. H. A. Plimmer, D.Sc., and F. G. Hopkins, M.A., M.B., D.Sc., F.R.S. London, New York, Bombay and Calcutta: Longmans, Green & Co. pp. viii + 168. Price, $1.50.

This is, probably, the most interesting and readable production in its line, since Johnson's "How Crops Feed" and "How Crops Grow." Written by the present Director of the famous Rothamsted Station and primarily for an English audience, it will nevertheless make a strong appeal to every one interested in the principles of agriculture, wherever they may be. It should have a wide field of usefulness.

It will appeal to the tyro because of the very attractive style in which the subject matter is presented, and because of the evident sincerity of the author, manifested strikingly in his judicial attitude toward the polemics with which the literature is fairly rife. To the expert the book will appeal, not only for the qualities just mentioned, but more for its suggestiveness.

Page after page will present paragraphs which, if they do not incite direct disagreement with the author, will at least suggest argument. There is a strong personality evidenced. An adequate review of the monograph would entail the writing of another (and perhaps larger) book. Consequently the present reviewer feels justified in calling particular attention to a few points only, while recording his judgment that Dr. Russell's book is of far more than ordinary scientific merit as well as interest.

Throughout the book and especially in the discussion of biological phenomena there is a clear recognition that all soil phenomena involve continuous changes. Yet, inconsistently, in discussing the "law of the minimum," "dominant factors," soil exhaustion and soil analyses there is evident an implicit assumption that the mineral factors in a soil do not change. In other words, a convincing array of data is marshalled showing that soil phenomena are all essentially dynamic in character, yet the discussion is mainly from a static point of view. It will be readily admitted by every one that, in any particular case, there may be a dominant factor or group of factors; but it does seem that the time has come when more progress would be made by recognizing, as a fundamental principle, that crop production is always the resultant of many variables, every one of which is interdependent with every other, and in consequence apparently "dominant" factors are of no more actual importance than each and every other factor.

Certain omissions from the discussion are surprising. One would expect, for instance, a discussion of the actual amounts of mineral ingredients (plant food) taken from and returned to the soil by plants during growth, the content at different stages of growth, and some notice of the work of Wilfarth, Römer and Wimmer,[1] and LeClerc and Breazeale.[2] Again, while one may agree with the author that the development of soil physics is lamentably unsatisfactory (pp. 85 *et seq.*), it does seem that a better case could be made for it. The significance of Mitscherlich's observations on the heat of wetting, the correlation of physical properties with the moisture con-

[1] Landw. Vers. Sta., **63**, 1 (1905).

[2] Year Book, U. S. Dept. Agr., **1908**, pp. 389–402.

tent of the soil, and the distribution of the rainfall in the soil are among the subjects which one might expect to find discussed and upon which it would be desirable to have Dr. Russell's views.

The discussion of soil colloids is not satisfying and creates the impression that they are a useful invention for bolstering otherwise troublesome arguments, rather than entities with which one can actually experiment. This is due in large part, of course, to the very hazy ideas generally prevailing regarding colloids and colloidal properties. Admitting that mineral colloids exist in the soil (for which no satisfactory evidence is given) it is certainly going too far to ascribe to them alone the adsorptive properties of the soil mass (pp. 54–58) as it is to claim from Way's work that "fixation" is essentially metathesis. The rather large body of conflicting evidence does not receive adequate attention.

The evident intention of fairness and the courtesy with which Dr. Russell has presented views with which he is not in accord have been noted above. However, a far from accurate presentation is given of the reviewer's own opinions regarding the composition and concentration of the soil solution and its relation to the solid components of the soil on the one hand and the growing plant on the other. This matter has been discussed quite fully in the reviewer's own recent book, and more recently been restated in another form,[1] and cannot be discussed here. But as one who has had a considerable part in the development of what Dr. Russell designates the "Whitney School," the reviewer feels obliged to record that his views are not accurately described by the references and discussion in the present book. For instance, the Whitney School(?) holds much the same attitude towards the hypothesis of toxic organic plant excreta that Dr. Russell holds toward the bacteria-protozoa theory, i. e., it may be "one of the factors....limiting....fertility in ordinary soils" (p. 118). It is far more important to recognize that organic substances exist in soils, sometimes injurious to plants, whatever may be their origin, by excretion, by cell sloughing or by secondary decomposition of organic débris.

On the whole the discussion of chemical principles involved in soil phenomena is rather meager. But analytical data are frequently given and the time-worn subject of soil analysis comes in for further discussion. It appears that, on the whole, Dr. Russell thinks that sometimes it might be worth while, but the candid reader will probably find it hard to see why. A strong argument is advanced for soil surveys under governmental auspices.

[1] Proc. 8th Int. Cong. Appl. Chem., Vol. 15.

The text is unusually free from mechanical and typographical errors, though a few were noted. Valuable (p. 24) should be variable. Hydrolysable (p. 31) will grate on some ears. A selected bibliography and reference list is a very valuable feature of the monograph, and there is also a satisfactory subject index.

FRANK K. CAMERON

TRAITÉ DE METALLOGRAPHIE. Par FÉLIX ROBIN. Préface de M. F. OSMOND. Paris: Libraire Scientifique A. Herman et Fils. 1912. pp. 464. Price, Fr. 30.00.

The author has produced a book which is a curious combination of much that is good and appropriate to the proper study of metallography, and much that has little, if any, bearing on the subject as it is ordinarily understood. He has included chapters on certain subjects such as hardness, compression figures, micro-chemical analysis, which are usually more appropriately treated in books on mineralogy. There is further a rather remarkable blending of material which can be spoken of as academic and practical. The practical side of the subject has been much more satisfactorily and extensively developed than is customary and it will be welcomed on this account, although the material is not so classified as to be easily found. The equilibrium diagrams are both good and bad. Some represent the latest development while others are quite ancient. Some of the more recent developments in diagrams are taken from German sources without changing the German wording; others are old French diagrams which are reproduced in spite of the fact that more reliable data were available. As usual with French books there has been little tendency to give full bibliographic references, but in some respects this is an improvement upon the average. The photographic reproductions are many and very good, and some of the composite photographs excellent.

A résumé of chapter headings would give one little idea of what the book actually contains. The author treats inadequately the history of the science and the subject of equilibrium diagrams; gives a good idea of the preparation and examination of specimens for microscopic study; discusses fully and satisfactorily the micrographic constituents of steels and irons, with considerable comment upon the effect of work, impurities, etc., upon the physical properties. Alloy steels, the brasses, bronzes, and other copper alloys are discussed, and there is a chapter on slags.

The book will be of most service to those interested in the metallography of steels.

HENRY FAY

A Dictionary of Applied Chemistry. By Sir Edward Thorpe, C.B., LL.D., F.R.S., Emeritus Professor of Chemistry, Imperial College of Science and Technology, South Kensington, London, assisted by Eminent Contributors. Revised and enlarged edition in five volumes. Vol. III, Gr-Oils. With illustrations. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. viii + 789. Price, $13.50.

The first two volumes of the new edition of this very valuable work have been recently reviewed in these columns;[1] and it is gratifying that the publishers are making such rapid progress with this new issue. No change in the plan or arrangement of subject matter is noted from the scheme adopted for the two volumes already issued, and as before many prominent names are found in the list of some thirty-six contributors.

Within the alphabetical range included in this volume, there are one hundred and forty new topics not included in the old edition. Of these the following are some of the more important: Guanidine; Gypsum; Haematite; Halogen-acetic Acids; Helium; Histidine; Hydrastine; Hydrolysis; Indanthrene Dyes; Indene; Indigo, Artificial, and Indigoid Dyestuffs; Indoxyl Compounds; Invertase; Ionium; Iridium; Isoprene; Ivory; Ketenes; Krypton; Lacquer; Lactones; Lanthanum; Lard; Lipase; Liquefaction of Gases; Liqueurs and Cordials; Lutecium; Maize and Maize Oil; Malonic Acid; Maltase; Martensite; Meat Extract; Mercaptans; Mercerizing; Metallography; Neat's Foot Oil; Neodymium; Neon; Nigrisin; Niton; Nitranilines; Nitriles.

About seventy topics included in the old edition have been rewritten and much enlarged, the more important being as follows: Graphite (but artificial graphite receives scant notice); Guaiacol; Gums, (including new matter on Suakin, Morocco, Aden and Australian or Wattle gums); Hydrazines; Hydrazones; Hydrogen Peroxide; Hypoxanthine or Sarcine; Indigo, Natural; Indium; Iron; Ketones; Lactic Acid; Lactones; Leucine; Lithium; Logwood; Lubricants; Margarine; Matches; Methyl; Molybdenum; Monazite; Naphthalene; Nitrogen, Atmospheric, Utilization of; Nitric Acid, Manufacture of; Oils, Essential; Oils, Fixed.

The references to original papers and general tenor of these articles appear to bring the subjects up to about the end of 1910. The rare gases, Helium, Krypton, and Neon, and also the recently discovered Niton, are considered in interesting paragraphs. An excellent digest is given of the principles of Hydrolysis, as illustrated by the ordinary types, viz., hydrolysis of metallic salts, of esters, of acyl derivatives (acid chlorides, amides, etc.), of complex carbohydrates (di- and polysaccharoses and glucosides); also a discussion of the effect of neu-

[1] This Journal, **48**, 191, 259.

tral salts in hydrolytic reactions, of enzyme action in inducing these processes, and finally those reactions in which alcohols play similar parts. A brief article on Indanthrene and the new class of "vat dyes" grouped with it affords information on the methods of preparation, constitution and properties of these valuable colors. Artificial Indigo, and the related Indigoid Dyestuffs, occupies about five pages; here is also shown the far-reaching consequences of the manufacture of this new material upon the well-established processes of production and application of the other artificial dyestuffs.

About eight pages are given to a discussion of the Lactones, the methods of preparing them, with many structural formulas, the properties of the several classes of lactones, and special consideration of a few of the important ones, such as *meconin, coumarin, umbelliferone, daphnetin* and *aesculatin*. Under the topic Lard are found the definitions of the various brands of edible lard, as established by the Rules of the Chicago Board of Trade; also the mode of preparation, properties and uses of each brand. A paragraph is also devoted to Lard Substitutes.

The topic of Lead includes a subsection devoted to the Lead Compounds Used in the Arts, in which is a good description of White Lead making by the Dutch-English method, but the newer, more rapid methods, such as the Carter process, receive meager mention, while the old, generally abandoned Milner process is given more than a column. Among white lead substitutes, lead sulphate produced from furnace fume is described as Hannay's White Lead; the product appears to be essentially the same as the "sublimed white lead" made by the Picher process. It is surprising that no reference is made to the legislation lately enacted by various countries, restricting or even prohibiting (in France since 1910) the manufacture or use of white lead.

The Liquefaction of Gases gives an excellent summary of the work of the pioneers in this field: beginning with the comparatively little known studies of "gases" and "vapors" by van Helmont, Boerhaave, Dalton, Monge, Clouet and Northmore, previous to 1806, next follows Faraday's important work in 1823 and 1845, Andrews' in 1869 and 1876 and van der Waals' in 1879. The liquefaction of the "permanent" gases, oxygen and carbon monoxide, by Pictet and Cailletet in 1877 led to experiments by Wroblewski, Dewar and others, and finally in 1895 Hampsen and von Lindé devised methods of "self-intensive" refrigeration, and produced liquid air in large quantity. Many references to original publications are given. Under Meat Extracts is an interesting sketch of Liebig's connection

with the industrial manufacture of this material. The article also includes the methods of testing and analysis of meat extracts. Metallography fills some twenty-one pages, and two full-page plates are included, showing the micro-structure of pure metals and alloys. Typical cooling "curves" and equilibrium diagrams of various classes of alloys, e. g., copper-nickel, copper-zinc, lead-tin, etc., are explained; deformation, fracture, and fatigue in metals are also considered.

In the chapter on Iron a sketch of a modern blast furnace has been included, and the new special steels containing nickel, chromium, aluminium, tungsten, and rarer elements are considered; also the Talbot steel process. Leather is mainly devoted to the old vegetable tannage processes, while chrome tannage, so important in this country, receives but a few lines with no adequate description. Nor is much consideration given to the replacement of hand labor in the beam house by machines, nor to the devices for accelerating the tanning process. And the use of organic acids, such as formic and lactic, for deliming hides and skins is barely mentioned. But the methods of analysis of tanning materials receive considerable attention.

Under Matches the list of paste compositions, and of patent applications for match machinery, of the old edition have been eliminated, and an illustrated account of the manufacture as conducted in the works of Bryant and May, Ltd., of London and Liverpool, is included. Many of these illustrations are too small to add materially to the value of the article. All European countries and Japan have adopted laws prohibiting, or at least closely regulating, the use of white or yellow phosphorus in matches. One reads further, "Only in the United States is there no legislation relating to the manufacture or use of matches made with white or yellow phosphorus." It is stated that the common double-tip match used here contains as much as 20 per cent. of white phosphorus, and generates 40–50 per cent. more phosphorus oxide vapor during the process of manufacture than does the ordinary match. Also it appears that the "warmth and humidity of the American climate increase the danger to the workers."

The longest contribution in the volume is that on Naphthalene and its derivatives, comprising 101 pages. Copious references to original literature make this valuable in the organic industrial field.

A good account of the Lindé method of obtaining nitrogen from the air, with a diagram of the apparatus, opens the important subject of Nitrogen and its compounds. The Utilization of Atmospheric Nitrogen, which has assumed such import-

ance since the appearance of the first edition of the work, is excellently presented, and illustrated by numerous diagrams and views in the various factories. The manufacture of calcium cyanoamide (nitrolim), cyanides, ammonia (Haber's process) and nitric acid by the Birkeland-Eyde, Schoenherr, and Pauling methods are included. The Manufacture of Nitric Acid (from sodium nitrate and sulphuric acid), by Professor Edward Hart of Easton, Pa., is the only contribution to this volume from America. In this are given the latest devices for carrying on the process, each illustrated by a diagram.

As in the preceding volumes, the care exercised in editing and publishing has maintianed the high standard of the work.

F. H. Thorp

Die Industrie der Steinkohlenteers und des Ammoniaks. Von Dr. G. Lunge und Dr. H. Köhler. Fünfte gänzlich umgearbeitete Auflage. Erster Band: Steinkohlenteer. Mit 354 eingedruckten Abbildungen. s. xviii + 1040. Preis: geh., M. 29.00; geb., M. 30.50. Zweiter Band: Ammoniak. Mit 163 Abbildungen im Text und auf 6 Tafeln. s. xii + 476. Preis: geh., M. 15.00; geb., M. 16.50. Neues Handbuch der chemischen Technologie (Bolley's chemische Technologie, dritte Folge), herausgegeben von Dr. C. Engler, wirkl, geh. Rat und Professor an der Technischen Hochschule Friedericiana in Karlsruhe. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1912.

The fourth edition of this standard work appeared in 1900, since which time the great development of the by-product coke oven has occurred and in consequence the coal-tar and ammonia industry has not only enormously developed, but has widened greatly in its scope. As against 702 pages in the fourth edition of the volume on coal tar, 1040 pages are now devoted to this subject and the 323 pages of the earlier volume on ammonia have grown to 476 pages in the edition now published.

Nor does this consist simply of additional matter, supplementary to the old. The authors state that, as they wished to discuss the new material with proper fullness, they have cut out much of the description of older processes and referred the reader, whenever it seemed necessary, by a note to the 4th edition.

The first considerable expansion of the subject matter is found in the section on the production of tar as a by-product in the manufacture of coke. Instead of 49 pages, which were given in the previous edition, we have now 107 pages. In this we find a very full and detailed account of the newer forms of by-product ovens such as the Semet-Solvay, the several forms of the Otto oven, the Koppers, the Brunck and the Coppeé ovens. What is of great interest is the account of the development of the extraction of benzene from coke-oven gases which has revolutionized the benzene industry and made possible

many additional utilizations of it other than in the color industry. Thus in 1908, the German benzene production amounted to 90,000 tons, of which 80,000 tons were extracted from coke-oven gases and 10,000 tons from coal and coke-oven tars. England, during the same year, produced 35,000 tons of benzene, chiefly from coal tar, France 13,000 tons and Belgium 6,000 tons.

Of course, it is in Germany that the by-product coke oven has developed most generally, so that at the present time 80 per cent. of German coke ovens are by-product ovens, from which tar and ammonia are collected; Belgium follows closely with 70 per cent. of its ovens by-product ovens, while in England and the United States the proportion has only risen to 16.6 per cent. The manufacture of water-gas tar and oil-gas tar, both relatively newer products, is quite fully described and their respective characters as compared with gas-retort tar discussed. In this connection, tables of comparative analyses of tars of various types, submitted with a paper prepared by the late Dr. H. W. Jayne for the London International Congress of Applied Chemistry in 1909, are given.

Among the uses for coal tar as such, we find described in this edition the treatment of roads and the production of a tar-macadam coating for roads to allay or do away with the dust nuisance. This has been extensively practiced in the last ten years in France and in England and to some degree in Germany. The only reference to the utilization of tar for the improvement of roads in the United States is the statement on the authority of J. D. Pennock that in 1903 16,000 tons of tar were so used. The use of materials like "Tarvia," a coal-tar preparation for road treatment, and of California asphaltic residuums has, however, attained very large proportions in this country.

As might be expected, the section on the analysis and valuation of the tar samples is much enlarged and improved and recent methods are described and illustrated. As an example of this, we would call attention to the discussion of the question of "free carbon" in tar and the importance of its correct determination.

The use of coal-tar pitch as a binder in the manufacture of coal briquettes, which has become a very large industry in Germany, Belgium and France, is described and illustrated and its importance indicated by statistical tables.

The use of heavy or so-called creosote oil for the preservation of wood has advanced greatly in the past decade and this subject is very fully treated in the volume before us, the Rüping process, which has found great acceptance in Germany, being

very fully described and illustrated. By this process, while the cell walls become thoroughly coated with the creosote oil, the excess of oil is forced out by air which has been compressed in the center of the timbers and much less oil is required than by the older process.

The progress of wood preservation in the United States is also noted and its status as late as 1910 reviewed.

The statistics of coke and coal-tar production throughout the world are brought down almost to the date of the issue of the work by notes in the appendix.

Volume II on Ammonia has not only grown in size, as noted before, but contains much that is radically new, representing the important synthetic work in this line that has been accomplished in the past decade or so. Thus we have a brief mention of Haber's process for the synthesis of ammonia from nitrogen and hydrogen in the presence of catalyzing agents, which is now being developed by the Badische Anilin- und Soda-Fabrik, a fuller account of which was given by Prof. Bernthsen at the late Congress of Applied Chemistry in New York. We have next the synthesis of ammonia through the intervention of the nitrides and here a very full account of Serpek's very successful process with aluminum nitride is given, whereby pure ammonia and pure alumina are manufactured from bauxite. We have also the processes for the production of ammonia by the intervention of cyanides and of cyanoamide, now so extensively manufactured by Frank and Caro's process.

This new edition also devotes a large space to the subject of liquefied ammonia, which has assumed far greater importance commercially than was the case at the time the earlier edition appeared. This section is especially well illustrated, moreover, showing the mechanical side of the liquid ammonia industry, its compression, its storage and its transportation.

We must not fail to note in conclusion that the German type of the older edition has given place to the Latin characters and that the book is both printed and illustrated with that perfection of mechanical detail so well known in the scientific books of Vieweg and Son.

SAM. P. SADTLER

DAS HYDROSULFIT. Teil II. Anorganische, organische und technische Chemie des Hydrosulfits. Von DR. KARL JELLINEK, Privatdozent an der Technischen Hochschule zu Danzig. Mit 2 Kurven. Sonderausgabe aus der Sammlung chemischer and chemisch-technischer Vorträge, begründet von F. B. AHRENS, herausgegeben von Prof. DR. W. HERZ, Breslau. XVIII Band, 1–6 Hefte. Stuttgart: Verlag von Ferdinand Enke. 1912. pp. viii + 230. Price, M. 9.00.

The first volume, dealing with the theoretical chemistry

of hydrosulphite, has already been reviewed.[1] The second volume should recommend itself most highly to all who are interested in any way whatever in hydrosulphite chemistry. The subject is treated in a clear and comprehensive manner as follows: I. Inorganic Chemistry, pp. 1–78. II. Organic Chemistry, pp. 79–125. III. Technical Preparation of Hydrosulphite and its Derivatives, pp. 125–168. IV. Technical Applications of Hydrosulphite and its Derivatives, pp. 169–208. The last 22 pages of the book contain a list of commercial products, the bibliography complete to March 1912, a list of German patents, and a subject and author index.

No details of technical methods of preparation, etc., have as yet been published, and the author is therefore forced to rely upon patent specifications and claims. He estimates that the annual German hydrosulphite output has a value of several million marks. The technical price is about 2 marks per kilo.

WILLIAM C. BRAY

CHEMISCH-TECHNISCHES PRAKTIKUM. Uebungsbeispiele aus der chemisch-technischen Analyse für Studierende an technischen Hochschulen und Universitäten. Von DR. ING. WILHELM MOLDENHAUER, Privatdozent für Chemie an der Technischen Hochschule zu Darmstadt. Berlin: Gebrüder Borntraeger. pp. vii + 206. Price, M. 6.80.

In this work, which is intended for use in technical high schools and universities, the author has taken as examples of analytical processes used in technology such cases as have a practical bearing and are encountered in the daily work of a technical chemist. The methods are described in sufficient detail to enable one to carry out the determination without difficulty and the reactions involved and the uses and properties of the substances are often discussed. An idea of the scope of the work can be obtained from a list of some of the subjects treated: Coal, water, illuminating gas, sulphur, saltpeter, soda, fertilizers, iron ores, zinc ores, oils, fats, soaps, glycerol, etc.

J. E. G.

A TEXT-BOOK OF INORGANIC CHEMISTRY. By GEORGE SENTER, D.Sc. (Lond.), Ph.D., Lecturer on Chemistry at St. Mary's Hospital, University of London, Lecturer on Physical Chemistry, Cass Technical Institute, Oldgate, E. C. London; Methuen & Co., Ltd.; New York: D. Van Nostrand Co. 1911. pp. x + 583. Price, $1.75.

The author has, in this text book of nearly 600 pages, given us a clearly written descriptive inorganic chemistry in which the more important of the modern theories of chemistry, such as the Principles of Chemical Equilibrium, the Determination of Molecular Weights in Solution, Electrolysis and Electrolytic

[1] THIS JOURNAL, 48, 98 (1912).

Dissociation are introduced at an early stage and their applications illustrated in the rest of the book. Owing to the size of type used it has been possible to enter very fully into the chemistry of the elements and compounds, and produce an excellent book for students in inorganic chemistry. J. E. G.

ELEMENTARY CHEMICAL THEORY. By J. M. WADMORE, M.A. New York: D. Van Nostrand Co. 1912. pp. 275. Price, $1.50.

"Being unable to find a suitable elementary text book on Theoretical Chemistry the author has, with some reluctance, added to the already large number of text-books on elementary substances." He has, however, given us a very clear and logical treatment of the subject, presenting only those features which will enable the student to grasp the results of the work in various lines without being completely lost in the maze of details whose relative value and bearing he is not yet able to appreciate. A student who has studied chemistry for a year should find this book interesting and helpful. J. E. G.

DIE ANALYSE DER SELTENEN ERDEN UND DER ERDSÄUREN. Ceriterden, Yttererden, Zirkonerde und Thorerde, Titansäure, Niobsäure und Tantalsäure. Von PROF. DR. R. J. MEYER, Privatdozent an der Universität Berlin, und DR. O. HAUSER, Privatdozent an der Techn. Hochschule Berlin. Mit 14 Abbildungen und 31 Tabellen. Die Chemische Analyse. Sammlung von Einzeldarstellungen auf dem Gebiete der chemischen, technisch-chemischen und physikalisch-chemischen Analyse. Herausgegeben von DR. B. M. MARGOSCHES, Privatdozent an der Deutschen Technischen Hochschule Brünn. XIV–XV. Band. Stuttgart: Verlag von Ferdinand Enke. 1912. pp. 320. Price, M. 10.

This book is a very valuable contribution to the literature of the chemistry of the rarer elements, concerned as it is with the analytical chemistry of the rare earths and rare earth acids. The joint consideration of these two groups is most instructive because of their intimate association in nature in many minerals.

The reputation of the authors gives one much confidence in the character of the work, and the selection of material is excellent.

The importance of spectrum analysis is wisely emphasized and the frequent tabulation of the chief lines in the arc and spark spectra, as well as the clear plates showing absorption spectra, will prove most valuable to the student in this field of research.

Some important work by American chemists, such as the recent work of Hunter upon elementary titanium and of James upon the rare earths, might have been added with advantage.

PHILIP E. BROWNING

Vol. XLIX April, 1913 No. 4

AMERICAN

CHEMICAL JOURNAL

THE ABSORPTION OF LIGHT BY WATER CHANGED BY THE PRESENCE OF STRONGLY HYDRATED SALTS, AS SHOWN BY THE RADIOMICROMETER—NEW EVIDENCE FOR THE SOLVATE THEORY OF SOLUTION

By J. Sam Guy, E. J. Shaeffer and Harry C. Jones

(This investigation was carried out with the aid of a Grant generously awarded by the Carnegie Institution of Washington to H. C. Jones.)

The use of the radiomicrometer in studying the absorption spectra of certain substances has already been discussed by Jones and Guy.[1] The radiomicrometer was used in the study of absorption spectra of solutions, rather than the grating spectrograph and the photographic plate, because the radiomicrometer enabled us to measure not only the positions of the different lines and bands, but also to study quantitatively their intensity. Further, the radiomicrometer, as has already been pointed out, enables us to study the absorption spectra of solutions over a much greater range of wave lengths than the photographic method.

In building a radiomicrometer that would be adapted to this work, that is, with sufficient sensibility and with a short period, one of the greatest difficulties encountered was to ob-

[1] Physik. Z., **13**, 649 (1912).

tain copper wire free from iron. This was a necessity, since the presence of an appreciable quantity of iron in the copper gave rise to a "magnetic control" which rendered the instrument unstable and the zero point inconstant. This difficulty was for the most part overcome, due to the kindness of Messrs. Leeds and Northrup, of Philadelphia, and of R. W. Paul, of London. They both furnished us with copper wire so free from iron that the "magnetic control" could easily be regulated. By means of this wire and the thermoelectric junction already described,[1] a most sensitive radiomicrometer which at the same time had a very short period was built. Work with salts of neodymium and praseodymium, the results of which were recorded in the *Physikalische Zeitschrift*, was done with this instrument.

At the beginning of the present academic year the absorption spectra of solutions of a large number of salts of different metals were mapped out. The spectra of these salts were compared with the absorption of water, using the same depths of water as the water in the various solutions. It was soon found that the absorption of the solution was *less*, and in some cases *very much less*, than that of the layer of water having a depth equal to the depth of the water in the solution. The depth of water in the solution was determined from the concentration of the solution and from its specific gravity.

It is obvious that the above is a very remarkable fact. The dissolved substance could not have less than no absorption of light, the assumption having been made, up to this time, that in an aqueous solution the water present absorbs just as much as pure uncombined water. The above result is directly at variance with everything that was known at the time.

It became at once obvious that we could not measure the absorption spectrum of a solution, subtract from it the absorption due to water, and conclude that the remainder was the absorption due to the dissolved substance, since the water in the solution has very different absorption from an equal amount of pure, uncombined water.

[1] Physik. Z., **13**, 651 (1912).

We then carried out a number of experiments in cells whose depths could be easily and accurately adjusted, with different substances, in the following manner: We measured the absorption spectra of a number of different substances. We then measured the absorption spectra of water having the same depths of layer as the water in the solutions. We found that for certain substances the pure water was more opaque than the solutions, and for other substances the water was more transparent. The percentage transmission, that is, the deflection of the radiomicrometer for the solution, divided by the deflection for water, for the first named substances amounted to more than one hundred per cent. Pure water had a different absorption from an equal depth of water in the solution, and since this difference varied from one dissolved substance to another, it is obvious that this method was not the one to be followed. It would be very difficult, not to say impossible, to interpret the results obtained by dividing the radiomicrometer deflection for the solution by those for pure water. We should simply be obtaining the transmission of the solution in terms of pure water, which was not what was desired.

What we want to know is the actual absorption or transmission of the solution, and then that of pure water having a depth of layer that was just equal to that of the water in the solution. These two sets of results could then be compared with one another.

In this earlier work we had, however, noted that solutions of those substances which are largely hydrated are more transparent than pure water having the depths of the water in the solutions in question. Solutions of nonhydrated substances, or of only slightly hydrated substances, provided the substances themselves do not absorb light, are not more transparent than pure water having the same depths as the water in the solution.

It would seem from this observation that water combined with the dissolved substance had less absorption of light than pure, uncombined water. To test this quantitatively the following procedure was adopted:

A solution of the substance in question was prepared of known concentration and its specific gravity determined. This solution was placed in one cell, set to a depth of say 2 mm. Some of the same solution was then placed in another cell set to a depth of say 1 mm. Light of given, known wave length was then passed through the one solution and the deflection noted. Light of this same wave length was then passed through the other solution, and the deflection in this case also noted. The deflection produced when the deeper solution was in the path of the beam of light was then divided by the deflection produced when the shallower solution was in the path of the light, and this gave the absolute transmission of the solution of the substance in question of known concentration, having a depth of layer of 20 mm. This process was repeated for the different parts of the spectrum, changing the wave length of light from reading to reading by only a small amount. Light of any given wave length was always passed through the one solution, and then, at once, through the other solution of a different depth. The object in using the two depths of the same solution, and then dividing the deflection produced by the deeper layer by that obtained when the more shallow layer was in the path of the beam of light, was to eliminate any effect of reflection from the glass ends closing the cells containing the solutions, and also to eliminate any changes in the total amounts of energy sent through the solution, due to slight changes in the intensity of the Nernst glower.

From the specific gravity of the solution and its known concentration, the amount of water in a layer of the solution, say 21 cm. in depth, could easily be calculated. Similarly, the amount of water in a layer of the solution which was 1 mm. deep could also be calculated. Water was then introduced into the two cells, and these cells so adjusted that the difference in the depth of the two was exactly equal to the depth of the water in the layer of the solution which was 20 mm. deep.

The deflection for the water in the deeper cell was then read for any given wave length of light, and then, at once,

the deflection when the light was passed through the *more shallow* layer of water. The deflection for the deeper layer was divided by the deflection for the more shallow layer. This operation was repeated for the various wave lengths of light in the manner just described. The result was the absolute transmission for water with a depth of layer just equal to the depth of water in the solution in question.

The above results for the solution are plotted as one curve, and those for water having the same depth as the water in the solution as another curve, wave lengths being abscissas and transmission ordinates. A comparison of the two curves shows at once whether water in the free, uncombined condition or the same depth of water in the solution in question is the more transparent.

The data obtained by dividing the deflections produced by the deeper solutions by those for the more shallow, and, similarly, by those for water, are also given in the following tables. These are the data from which the accompanying curves were plotted.

The substances studied were chosen from the standpoint of their power to solvate or to combine with the solvent in which they were dissolved. In all of the work recorded in this paper the solvent used was water. We were practically limited, in this phase of the work, to those substances which themselves have little or no power to absorb light. We were limited to those substances that are both colorless in the visible part of the spectrum, and have little or no absorption in the regions in which the absorption bands of water occur.

We selected for these substances with little or no hydrating power salts of potassium and ammonium. The potassium salts studied were the chloride and nitrate. Ammonium chloride and nitrate were also investigated. We selected for the salts with large hydrating power calcium chloride, magnesium chloride and aluminium sulphate. These salts were shown by the earlier work in this laboratory, which was done shortly after Jones proposed the solvate theory of solutions, using the freezing-point method, to be among the most strongly hydrated substances with which we are familiar.

It will be seen from the following data that two depths of layers of each solution of every substance investigated were employed. The object of this was to bring out the two most important water bands in the region of the spectrum investigated. This could not be done by studying only one depth of solution, since the depth which was necessary and sufficient to bring out clearly one of these water bands would not bring the other out in the way desired. By using the two depths of solution and studying each of them in the manner described above, that is, by the differential method, we were able to investigate both of the water bands as produced, on the one hand, by the pure solvent, and, on the other, by the solution.

In the following tables, under λ are given the wave lengths of light that were passed through the solution, and under I/I_0 the percentage of transmission, on the one hand, of the solution, and, on the other, of water having a depth exactly equal to that of the water in the solution.

The ordinates of the curve, as has already been stated, are percentage transmissions and the abscissas wave lengths.

Table I

λ	KCl 4N I/I_0	H_2O	NH_4Cl 4 N I/I_0	H_2O	NH_4NO_3 3.12 N I/I_0	H_2O
710	97	97	92	98	95	98
724	96	95	91	96	97	98
741	95	95	90	92	96	96
760	93	95	85	92	91	95
776	92	95	85	88	92	94
798	94	95	88	95	91	95
818	92	95	87	95	92	96
836	94	93	87	95	91	94
855	91	90	86	93	89	92
878	92	90	86	91	90	93
900	90	89	84	87	89	88
922	87	86	82	86	85	90
947	82	84	79	82	82	83
958	77	78	73	72	73	79
964	75	73	69	70	70	71
969	65	65	64	63	65	67
974	58	56	57	58	58	59

Table I (continued)

979	51	50	52	52	50	54
982	47	46	45	46	44	46
985	41	45	43	43	40	44
991	39	43	41	43	39	43
1007	39	43	41	42	39	44
1013	40	42	39	44	41	44
1019	42	46	40	46	42	44
1025	41	42	44	49	45	48
1032	49	49	44	49	48	49
1037	53	52	56	55	52	53
1042	56	56	53	58	55	55
1046	59	60	57	57	57	60
1059	63	62	58	65	60	65
1065	68	67	62	67	64	65
1072	71	68	64	68	66	69
1078	74	72	67	67	66	72
1085	75	73	67	66	68	74
1100	77	75	68	72	69	78
1113	76	76	69	72	69	78
1138	75	72	68	70	68	72
1148	70	69	64	65	64	71
1158	64	63	62	64	59	64
1165	58	59	58	58	56	60
1172	52	51	50	50	53	52
1179	42	40	40	40	38	41
1186	29	28	29	26	29	30
1193	18	19	19	19	18	19
1200	13	16	14	13	12	17
1206	10	12	12	12	9	13
1213	10	11	10	12	9	13
1220	10	11	10	11	9	12
1227	10	11	10	11	9	12

In the above table the depth of layer of all the solutions was the difference between 21 and 1, i. e., 20 mm. The depth of water was in every case the same as that of the water in the solution in question.

The depth of layer of the following solutions was the difference between 11 mm. and 1 mm., i. e., 10 mm. The depth of water used was in every case the same as that of the water in the solution:

Table II

λ	KCl 4 N I/I_0	H_2O	NH_4Cl 4 N I/I_0	H_2O	NH_4NO_3 3.12 N I/I_0	H_2O
1085	85	86	79	87	81	88
1100	87	88	80	92	81	93
1113	86	87	79	86	84	86
1138	81	85	79	84	81	84
1148	79	82	77	84	78	84
1158	80	79	74	81	76	81
1165	76	77	71	77	72	77
1172	72	71	66	70	67	70
1179	64	62	59	62	61	62
1186	51	51	52	50	50	50
1193	41	43	42	44	40	44
1200	35	38	37	40	34	40
1206	37	36	35	37	32	37
1213	30	34	30	36	32	36
1220	30	35	29	35	34	35
1227	30	34	30	35	32	35
1233	30	33	28	35	31	35
1241	30	34	29	34	31	34
1248	31	34	28	33	31	33
1250	33	34	30	34	32	34
1255	34	35	30	36	32	36
1268	34	35	31	37	32	37
1270	37	31	32	38	33	38
1285	38	38	33	38	33	38
1295	39	38	32	38	33	38
1300	41	38	32	39	34	39
1308	42	39	32	41	35	41
1316	41	39	32	40	34	40
1323	42	37	32	38	34	38
1330	40	37	32	37	33	37
1338	40	35	30	35	31	35
1346	36	33	28	36	30	36
1352	34	29	26	29	27	29
1358	29	26	23	27	25	27
1365	25	22	21	23	21	23
1372	20	18	17	20	17	20
1387	13	12	12	11	10	11
1404	7	7	7	8	7	8
1418	3	4	4	3	3	3
1430	2	2	3	2	2	2
1445	0	0	0	1	1	1

In Table II the depth of layer of the solution that was used was only half of that in Table I. The object of this was to bring out more prominently the second water band.

The depth of layer of the following solutions was the difference between 21 mm. and 1 mm., i. e., 20 mm. The depth of water used in every case was the same as that of the water in the solution:

Table III

λ	$CaCl_2$ 5.38 N I/I_0	H_2O	$MgCl_2$ 4.96 N I/I_0	H_2O	$Al_2(SO_4)_3$ 1.02 N I/I_0	H_2O
710	94	98	95	98	95	93
724	92	98	98	98	95	95
741	90	95	95	98	94	93
760	87	94	94	98	92	93
776	88	93	92	97	93	95
798	91	96	93	94	92	90
818	93	99	90	90	93	92
836	92	97	92	95	92	92
855	90	93	91	90	90	91
878	90	90	91	93	91	90
900	89	92	88	92	89	90
922	86	91	88	91	85	86
947	87	84	84	86	82	81
858	78	79	76	78	76	73
964	75	73	82	76	72	66
969	70	68	75	69	68	61
974	65	62	68	65	64	55
979	59	53	61	56	58	48
982	51	49	48	51	53	42
985	48	49	54	45	51	40
991	44	46	48	49	47	39
1007	42	46	46	48	46	38
1013	42	46	45	50	46	39
1019	43	49	44	51	44	40
1025	47	50	46	44	46	43
1032	52	53	51	54	46	45
1037	55	55	52	56	52	50
1042	58	59	56	58	53	53
1046	62	62	59	65	55	55
1059	66	65	63	67	55	58
1065	71	70	69	70	62	63
1072	74	72	71	75	60	65
1078	75	74	71	76	64	69
1085	78	76	76	79	65	70

Table III (continued)

λ	$CaCl_2$ 5.38 N I/I_0	H_2O	$MgCl_2$ 4.96 N I/I_0	H_2O	$Al_2(SO_4)_3$ 1.02 N I/I_0	H_2O
1100	80	77	78	79	67	72
1113	79	78	80	81	67	74
1138	77	75	77	78	64	67
1148	74	71	75	77	60	65
1158	69	65	73	73	57	55
1165	66	62	65	65	55	53
1172	61	52	61	58	50	43
1179	54	41	52	44	45	34
1186	42	30	43	32	34	22
1193	32	21	32	24	25	15
1200	22	17	23	18	20	12
1206	16	16	18	17	16	10
1213	13	15	16	18	14	9
1220	12	13	14	15	11	10
1227	12	13	14	16	12	8

In the following table the depth of layer used was the difference between 11 and 1 mm., i. e., 10 mm. The object of using the smaller depth of the solution was to bring out more clearly in the case of hydrated salts the second water band:

Table IV

λ	$CaCl_2$ 5.38 *N* I/I_0	H_2O	$MgCl_2$ 4.96 N I/I_0	H_2O	$Al_2(SO_4)_3$ 1.02 N I/I_0	H_2O
1085	84	84	82	84	79	82
1100	84	84	83	84	78	81
1113	84	86	83	84	78	84
1138	86	85	82	83	77	83
1148	82	83	79	80	75	80
1158	80	79	77	77	73	77
1165	78	76	77	75	70	73
1172	76	72	74	70	66	69
1179	72	65	71	64	63	58
1186	63	55	62	52	55	48
1193	54	45	56	46	49	39
1200	45	40	48	42	43	34
1206	38	39	42	40	38	30
1213	35	39	39	38	36	29
1220	33	36	37	38	34	28
1227	32	36	36	38	32	28
1233	31	35	34	37	32	28

Table IV (continued)

1241	32	35	34	34	31	28
1248	32	35	34	37	31	28
1250	33	35	34	38	31	28
1255	33	37	34	38	31	28
1268	35	38	33	38	30	29
1270	37	39	34	39	30	30
1285	38	40	35	40	30	31
1295	40	40	35	40	30	32
1300	42	41	36	41	30	32
1308	42	41	37	42	30	33
1316	45	41	39	42	30	33
1323	47	40	39	41	28	33
1330	46	39	40	40	27	32
1338	45	37	38	38	27	30
1346	42	35	38	36	24	27
1352	40	32	34	33	22	24
1358	37	29	33	30	20	21
1365	33	25	29	26	18	19
1372	29	21	25	22	15	15
1387	19	13	18	15	10	9
1404	12	10	12	11	7	5
1418	7	6	7	9	4	3
1430	3	3	4	3	2	2
1445	2	1	1	1	1	1

When salts which are strongly hydrated in aqueous solution are not very concentrated, the difference between the transparency of the salt solution and that of water of the same depth of layer as the water in the solution is not so pronounced. This is what would be expected, since the total amount of water combined with the dissolved salt increases with the concentration of the solution. The data given in the following table bring out this fact:

Table V

λ	$CaCl_2$ 2.69 N I/I_0	H_2O	$MgCl_2$ 2.48 N I/I_0	H_2O	$Al_2(SO_4)_3$ 0.508 N I/I_0	H_2O
710	96	94	95	95	97	96
724	95	96	93	96	98	96
741	95	95	90	95	95	93
760	94	96	92	95	95	95
776	93	97	93	95	95	95
798	90	98	91	95	96	96

Table V (continued)

λ	$CaCl_2$ 2.69 N I/I_0	H_2O	$MgCl_2$ 2.48 N I/I_0	H_2O	$Al_2(SO_4)_3$ 0.508 N I/I_0	H_2O
818	93	97	91	93	95	96
836	91	96	89	93	93	95
855	91	92	88	92	92	92
878	90	92	84	90	90	91
900	88	90	84	88	89	86
922	89	92	81	86	82	85
947	82	86	78	83	78	80
958	75	79	72	76	73	75
964	70	74	70	73	68	69
969	65	69	62	64	62	62
974	58	61	58	58	57	54
979	50	52	50	51	50	46
982	44	47	46	46	46	42
985	40	43	42	43	43	40
991	39	41	40	41	41	39
1007	38	40	41	42	40	40
1013	39	42	40	44	40	40
1019	40	43	40	44	41	41
1025	43	45	44	41	43	43
1032	45	47	47	44	45	46
1037	48	50	50	46	47	48
1042	51	52	52	48	49	49
1046	56	56	56	54	53	54
1059	61	59	58	55	60	59
1065	65	64	64	62	59	62
1072	69	67	67	64	63	65
1078	70	69	69	67	65	69
1085	72	72	72	68	68	72
1100	73	73	73	71	69	73
1113	72	74	74	72	68	74
1138	72	74	74	70	67	72
1148	66	69	69	67	64	67
1158	67	62	62	60	58	62
1165	57	58	58	58	54	54
1172	52	51	53	52	47	46
1179	46	39	42	42	39	35
1186	30	27	31	27	28	25
1193	20	19	21	20	20	16
1200	13	14	15	15	14	12
1206	12	11	12	13	12	10
1203	11	11	12	12	11	10
1220	11	10	11	11	11	10
1227	10	9	10	10	10	9

The depth of layer of the different solutions for which the results are recorded in the above table was the difference between 21 and 1 mm., i. e., 20 mm. The results are, therefore, comparable with those recorded in Table III, the difference being a difference in the concentrations of the solutions used. It will be seen from a glance at the table that the difference between the transmission of the solution and that of water at the same depth as the water in the solution is very much less for the more dilute than for the more concentrated solutions. As has already been pointed out, this is exactly what would be expected in terms of the solvate theory applied to the phenomenon in question.

Considerable work was done in *comparing directly* the transmission of a solution and that of water having the same depth as the water in the solution in question. The deflection of the radiomicrometer as given by the solution is in the column marked "I sol." and the deflection as given by water having the same depth as water in the solution is given in the column marked "I_0 H_2O."

The results obtained for aluminium sulphate having a concentration 1.02 N and for 4 N potassium chloride are given in the following table. The depth fof solution used was 20 mm. and the depth of water that o the water in the solutions in question.

Table VI

λ	I sol. $Al_2(So_4)_3$	I_0 H_2O	I sol. KCl	I_0 H_2O
710	50	51	53	53
724	58	58	56	56
741	62	63	67	68
760	72	72	77	77
776	75	76	88	90
798	83	83	98	99
818	82	82	108	109
836	93	94	116	116
855	97	97	124	124
878	105	105	129	130
900	105	105	140	138
922	112	112	140	140
947	113	113	142	142
958	109	106	136	136

Table VI (continued)

λ	I sol. $Al_2(SO_4)_3$	I_0 H_2O	I sol. KCl	I_0 H_2O
964	107	100	129	125
969	104	93	118	116
974	98	83	108	106
979	93	73	92	92
982	82	66	83	83
985	80	64	78	80
991	78	62	78	80
1007	78	65	78	81
1013	74	65	81	85
1019	77	68	84	88
1025	80	75	96	96
1032	84	77	100	101
1037	91	84	112	108
1042	92	92	119	116
1046	99	99	125	120
1059	105	105	141	136
1065	109	112	150	145
1072	114	119	159	153
1078	118	125	164	158
1085	122	132	168	164
1100	128	140	176	172
1113	129	142	178	175
1138	127	142	174	170
1148	123	131	164	162
1158	112	118	161	159
1165	108	111	157	154
1172	99	94	132	126
1179	87	74	107	100
1186	68	49	73	66
1193	54	35	50	48
1200	42	26	24	36
1206	35	23	39	32
1213	30	21	25	30
1220	28	20	24	29
1227	26	19	24	28
1241	24	19	23	26
1255	23	18	25	27

In this work duplicate measurements were made with the radiomicrometer for nearly every solution of all the substances worked with at the various wave lengths studied. It was found that the readings for the different

solutions of the same substance having the same concentration were, for a given wave length, different from one another to the extent of somewhat less than 2 per cent. From this it seems fair to assume that the error in our work was not greater than 2 per cent.

An examination of the tables of data for potassium chloride, ammonium chloride and ammonium nitrate, that is, for those substances which, in aqueous solutions, combine with very little water, as was demonstrated by the freezing-point method, shows that for all wave lengths studied the solution and water of the same depth as the water in the solution have practically the same transmission. The dissolved substance does not combine with the solvent water, and the water in the solution has almost exactly the same effect upon light as so much pure water would have. This is exactly what would be expected from our knowledge of the absorption of light by dissolved substances and by the solvent. When we began this work we supposed that the water in the solution, whether it was combined with the dissolved substance or not, would have the same power to absorb light as so much pure solvent water. We shall now see that such is not the case.

The results for the above named substances were not plotted in the form of curves, since the curve for water and for the solution would practically coincide with one another, the dissolved substance having very little absorption over the region of wave lengths studied in this investigation.

When we turn to the data in Tables III and IV very different relations manifest themselves. These are the data for calcium chloride, magnesium chloride and aluminium sulphate, that is, for salts which, in aqueous solution, are strongly hydrated, as was shown by the earlier work in this laboratory.[1] The solution in these cases is often more transparent than the same amount of water that is contained in the solution.

That these relations may appear the more clearly, the results obtained for the above named salts are plotted as curves in Figs. I to VI. Fig. I is the curve for calcium chloride

[1] Carnegie Institution of Washington, Publication No. **60**.

having a depth of 20 mm. This was obtained by dividing the deflection produced by 21 mm. of the solution by that produced by 1 mm. of the solution. On the same sheet we have the curve for water having a depth equal to that of the water in the calcium chloride. This curve for water was also obtained by the "differential" method, i. e., by dividing the deflections produced by the deeper solution by those obtained with the more shallow solution, the difference in the depths of water in the two cases being just equal to the depth of water in 20 mm. of the solution in question. Fig. II is the curve for calcium chloride with a depth of layer of 10 mm. (11–1). The data from which the curve was plotted are contained in Table IV. The smaller depth of solution was used so that the water band between 1.2μ and 1.3μ would come out more distinctly. The results for this solution, like those for all the others, are compared with the absorption of a depth of water equal to that of the water in the solution. The absorption of the water in this, as in all other cases, was obtained by the "differential" method.

Fig. III is the curve for magnesium chloride having a depth of 21 — 1 = 20 mm. and the corresponding water curve. The data from which these curves are plotted are given in Table III.

Fig. IV is the curve for magnesium chloride having a depth of 1 cm., also obtained by the "differential" method. These data are taken from Table IV.

Fig. V is the curve for aluminium sulphate having a depth of 21 — 1 = 20 mm. and the corresponding absorption curve for water.

Fig. VI is the curve for aluminium sulphate having a depth of 11 — 1 = 10 mm. and the corresponding water curve.

Fig. I shows the relative absorption of water and of the solution of calcium chloride having a concentration of 5.3 normal and a depth of 20 mm. The corresponding water curve is marked throughout by the symbol "H_2O." The solution is the more transparent from 0.9μ to nearly 1μ. The water then becomes the more transparent over a short region of wave lengths. From 1.05μ to 1.2μ the solution is

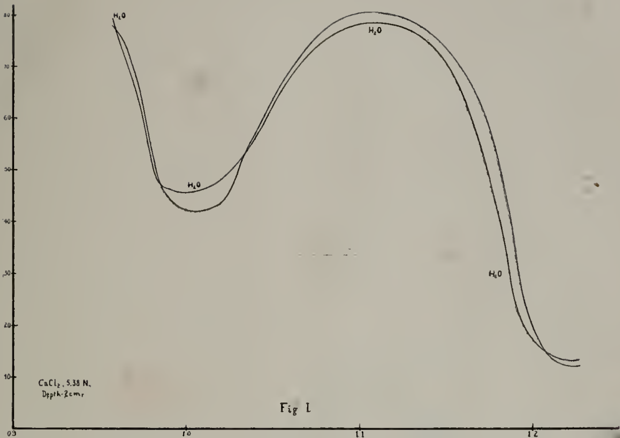

H$_2$O
H$_2$O
H$_2$O
H$_2$O
CaCl$_2$, 5.38 N.
Depth-2cms

Fig I

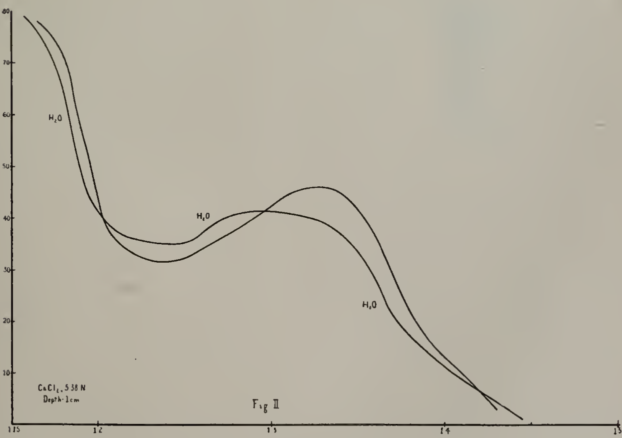

H$_2$O
H$_2$O
H$_2$O
CaCl$_2$, 5.38 N
Depth-1cm

Fig II

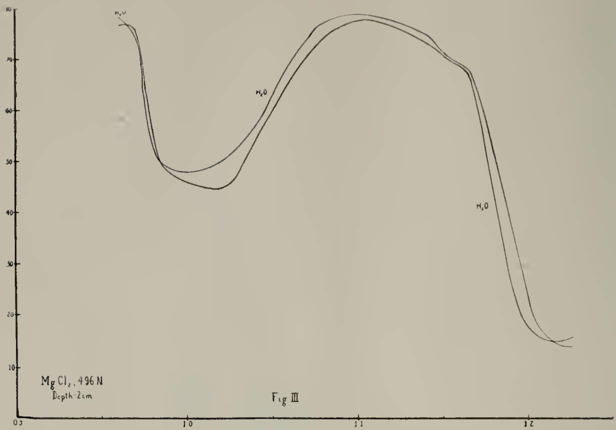


Fig III

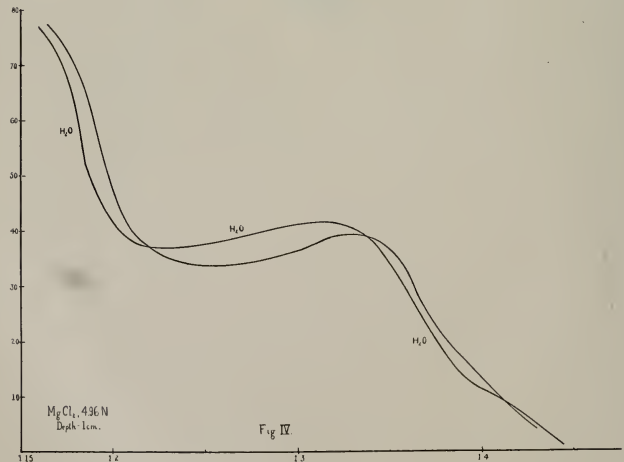


Fig IV.

the more transparent. In this region the solution becomes as much as 25 per cent. more transparent than the pure water, as can be seen by comparing the points on the "water" curve with the corresponding points on the curve for the solutions which are vertically above the points on the water curve. The water becomes appreciably more transparent only at and near the bottom of the "water band" having a wave length of approximately 1μ. This is the effect that we would expect to get if the dissolved substance exerted a "damping" effect on the absorption of light by water.

It will be recalled that the salts which do not form hydrates show, in aqueous solution, practically the same absorption as the corresponding amount of water. It would, therefore, seem reasonable to account for the differences in the case of nonhydrating and strongly hydrating salts as due to the water of hydration, or the water that, in this case, is combined with the calcium chloride.

The curves in Fig. II are for a smaller depth of the same solution of calcium chloride. This figure brings out the same general relations as was shown in Fig. I. The water curve in the region 1.25μ is above that of the solution, showing that water in this region for the more shallow depth of solution is more transparent than the solution. The additional feature brought out by this figure is the water band in the region 1.4 to 1.5μ. After the first named water band is passed the solution becomes more transparent than the water, and remains so until the wave length 1.42μ is reached. Here both the solution and the water are practically opaque as is shown by both the curves approaching the abscissas.

The curve for magnesium chloride having a depth of 20 mm. is almost exactly a duplicate of that for calcium chloride having the same depth. Practically the only difference worthy of mention is in the region from 1.0μ to 1.1μ. In the case of magnesium chloride the water remains the more transparent over this region of wave lengths. In the case of calcium chloride the solution is the more transparent over this region. The difference in the transparency of the water and the solution throughout the region is, however, not very great. From

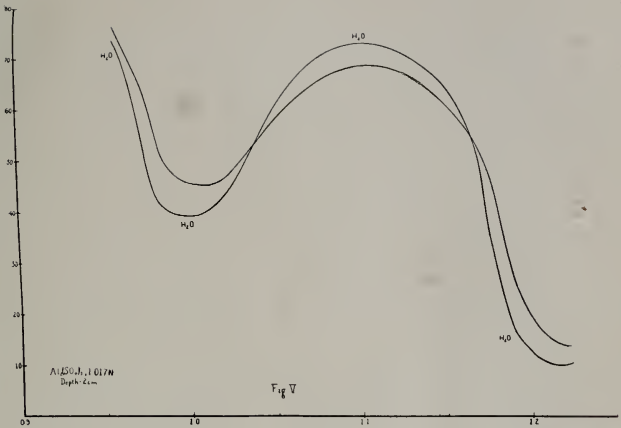
1.1μ towards the longer wave lengths, as we come down the descending arm of the curve towards the second water band, the water in the case of the magnesium chloride, as in the case of calcium chloride, becomes much more transparent than the solution, the differences here being of the same order of magnitude as those with calcium chloride.

Fig. IV gives the results for magnesium chloride with a depth of layer of 1 cm. The same relations hold in Fig. IV as in Fig. III, for the relative transparency of the water and of the solution. The water becomes the more transparent from 1.22μ to 1.34μ. For the longer wave lengths the solution becomes more transparent until the region 1.41μ is passed. For wave lengths longer than 1.41μ the transmission of both solution and water is practically zero, that is, they both become opaque to the longer wave lengths.

The results in Fig. V bring out some new features of interest and importance. These are the results that were obtained with aluminium sulphate. The new feature shown by the curve for aluminium sulphate, as compared with those for calcium chloride and magnesium chloride, is that at the minimum of the curve corresponding to wave length 1μ the solution is more transparent than the corresponding water. Beyond the wave length 1.04μ the water becomes the more transparent with aluminium sulphate as with magnesium chloride. Beyond the wave length 1.06μ the solution becomes more transparent in this case as with magnesium chloride and calcium chloride.

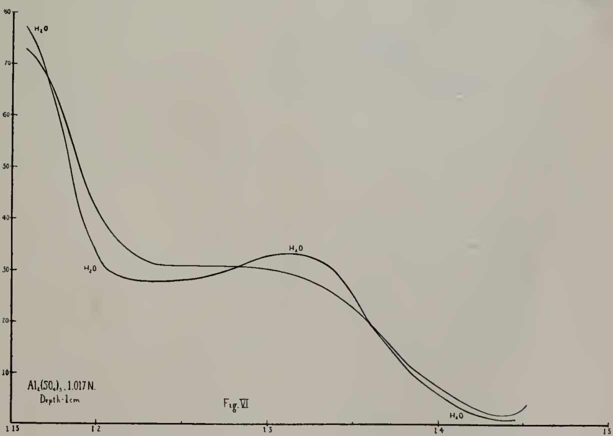
If we turn to Fig. VI the relations are as follows: In the region of 1.2μ the water is the more opaque. From 1.209μ to 1.306μ the water becomes the more transparent. From 1.306μ to the longest wave length studied, the solution again becomes more transparent than the corresponding layer of water.

An examination of all the results thus far obtained bearing on this problem leads us to conclude that the greater transparency of the solution as compared with the water in the solution must be due to some action of the dissolved sub-



80
70
60
50
40
30
20
10
0.9
1.0
1.1
1.2
H_2O
H_2O
H_2O
H_2O
$Al_2(SO_4)_3$, 1.017 N
Depth - 2 cm

Fig. V



80
70
60
50
40
30
20
10
1.15
1.2
1.3
1.4
1.5
H_2O
H_2O
H_2O
H_2O
$Al_2(SO_4)_3$, 1.017 N.
Depth - 1 cm

Fig. VI

stance on the solvent water. The question remains, what is this action?

We have seen from our earlier work on the absorption spectra of solutions, which has been in progress in this laboratory continuously for the past eight years, that the solvent can have a marked effect on the power of the dissolved substance to absorb light. This was first shown by Jones and Anderson,[1] and a large number of examples of this effect have since been found by Jones and Strong.[2] We interpreted the effect of the solvent on the power of the dissolved substance to absorb light as due to a combination between a part of the liquid present and the dissolved substance. This enabled us to explain a large number of facts that were brought to light for the first time by the investigations of the absorption spectra of solutions which have been carried on in this laboratory. Many of the phenomena which were thus explained, it seemed, could not be explained in terms of any other suggestion that has thus far been made. In a word, the solvate theory of solution, as proposed by Jones about a dozen years ago[3] to supplement the theory of electrolytic dissociation in order that we might have a theory of the real solutions which we use in the laboratory, and not simply a theory of ideal solutions as the theory of electrolytic dissociation alone must be regarded, has served good purpose in explaining the phenomena that have been previously observed in connection with the absorption of light by solutions of dissolved substances.

We are inclined to explain the phenomena recorded in this paper by means of the same theory. For solutions of those substances which have been shown by entirely different methods not to hydrate to any appreciable extent, the absorption of light by the solution and by a layer of water equal in depth to that of the water in the solution is, to within almost the limit of experimental error, the same.

For those substances which have been shown to form com-

[1] Carnegie Institution of Washington, Publication No. **110**.

[2] *Ibid.*, Nos. **130** and **160**.

[3] This Journal, **23**, 89 (1900).

plex hydrates, however, the absorption of light by their solutions and by a layer of water equal in depth to that of the water in the solution is very different. The water in these solutions is usually more opaque to light than the solution, or, what is the same thing in other words, a solution is more transparent than the water that is present in the solution.

The most rational explanation of this phenomenon appears to us to be that the part of the water that is combined with the dissolved substance has a smaller power to absorb light than pure, free, uncombined water. The fact that we are able to detect the difference between the water in the solution and pure water, by its action on light, we regard as good evidence in favor of the water in the solution being different from pure, free water. This difference, it seems to us, can be readily accounted for by the fact that a part of the water present in the solution is in combination with the dissolved substance.

We have carried out similar investigations with aluminium nitrate, but the concentration of the strongest solution that could be obtained was not sufficiently great to show the phenomenon in question. We, therefore, do not incorporate the results obtained with this substance. That the solutions must be very concentrated to show clearly the phenomenon with which we are dealing is shown by the results given in Table V. Here the solutions of the three salts in question that were used are more dilute than those for which the results are tabulated in Tables III and IV. An examination of this table will show that the phenomenon in question does not manifest itself to anything like the same extent as with the more concentrated solutions. This is exactly what we would expect in terms of the solvate theory of solutions. The more concentrated the solution the larger the total amount of the water present combined with the dissolved substance. If combination between water and the dissolved substance explains the facts recorded in this paper, then the larger the amount of water present that is combined with the dissolved substance, the more pronounced the phenomenon in question.

The results obtained with aluminium sulphate bring out the same facts shown by calcium chloride and magnesium

chloride. They, however, show in addition that water is more transparent in the region 1.1μ and more opaque at 1μ. That the sulphate should not agree throughout with the chlorides is really not surprising, since the sulphates show abnormal results in almost every particular. This is probably due, in part at least, to the large amount of polymerization which the sulphate molecules in general undergo in the presence of even water as a solvent. It should also be remembered in the present connection that, while calcium chloride and magnesium chloride crystallize with only six molecules of water, and are, therefore, only largely hydrated, aluminium sulphate crystallizes with 18 molecules of water and is, therefore, very largely hydrated.

The results in Table VI are, as has already been stated, the radiomicrometer deflections for a solution of aluminium sulphate and those for water having the same depth as the water in the solution in question, and the corresponding data for potassium chloride. A comparison of the two columns for potassium chloride and its corresponding water shows that the two are almost equally transparent to all the wave lengths studied.

A comparison of aluminium sulphate with its corresponding water brings out the phenomenon that we are now discussing in a very pronounced manner. It is for this reason that the data in this paper are given.

One other relation of a general character should be pointed out. The curves upon all six of the figures show that the addition of salt to water shifts the absorption towards the longer wave lengths. This is analogous to what has already been found by Jones and Uhler,[1] Jones and Anderson,[2] Jones and Strong,[3] and Guy and Jones,[4] when the absorption of salts as affected by the water present was studied. It was found that rise in temperature and increase in the concentration of the solution both tended to shift the absorption of the

[1] Carnegie Institution of Washington, Publication No. **60**.

[2] *Ibid.*, Publication No. **110**.

[3] *Ibid.*, Publications No. **130** and No. **160**.

[4] This Journal, **49**, 1 (1913).

salt towards the longer wave lengths. The effect of rise in temperature and the increase in the concentration of the solution tended to simplify the hydrates in combination with the particles of the salt. The resonator within this simplified system seems to vibrate so as to shift the absorption bands towards the red.

The effect of the salt on the absorption of the water is the same as that of rise of temperature and increase of concentration on the absorption of the dissolved substance. We should naturally look for a similar explanation of the two sets of phenomena. It has been suggested by Dr. Guy that the effect of the salt on the absorption of light by water may be due to the breaking down of the associated molecules of water by the dissolved substance. This would be in keeping with the discovery made by Jones and Murray,[1] that one associated substance when dissolved in another associated substance diminishes its association.

In terms of this explanation, however, it is a little difficult to see why nonhydrated salts, such as were used in this work, do not also diminish the association of water and cause a shifting of its absorption bands towards the longer wave lengths. It may be that the effect of the dissolved substance in breaking down the association of the water is pronounced only in the case of water of hydration or the water that is combined with the dissolved substance, and that the explanation offered above is fundamentally correct.

In conclusion we wish to express our thanks to Professor A. H. Pfund, who has made many valuable suggestions during the progress of this work. We would also express our thanks to Dr. E. P. Wightman, who has kindly drawn the curves for us.

Johns Hopkins University
December, 1912

[1] This Journal, **30**, 193 (1903).

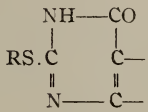
[Contributions from the Sheffield Laboratory of Yale University]

CCVII—RESEARCHES ON PYRIMIDINES ALKYLATION WITH BENZYL CHLORIDE

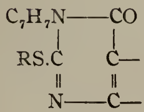
By Treat B. Johnson and Zai Ziang Zee

[SIXTIETH PAPER]

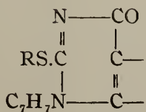
Every 2-mercapto-6-oxypyrimidine (I) which we have so far examined in this laboratory has undergone alkylation smoothly with benzyl chloride, in the presence of sodium ethylate, giving the corresponding N-benzyl derivatives, (II) or (III). In only one case have we observed the formation of an imido ester derivative corresponding to formula (IV).



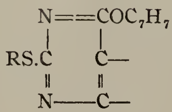
(I)



(II)



(III)

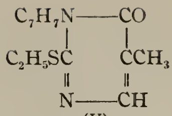


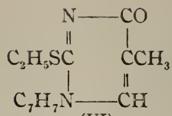
(IV)

2-Ethylmercapto-6-oxypyrimidine reacted with this halide, giving a mixture of the corresponding 1- and 3-benzylpyrimidines, while from 2-ethylmercapto-5-bromo-6-oxypyrimidine only a 3-benzyl derivative was isolated. The yield of this was, however, 60 per cent. of the theoretical.[1] From 2-ethylmercapto-5-methyl-6-oxypyrimidine[2] we obtained a yield of the N-benzylpyrimidines, (V) and (VI), corresponding to about 90 per cent. of the calculated amount, and 68 per cent. of this was the 3-benzylpyrimidine represented by formula (VI). Analogous results were obtained by alkylation of

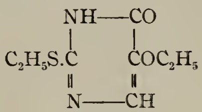
[1] Johnson and Derby: This Journal, **40**, 444.

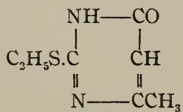
[2] Johnson and Derby: *Loc. cit.*


(V)


(VI)

2-ethylmercapto-5-ethoxy-6-oxypyrimidine[1] (VII), but 2-ethylmercapto-4-methyl-6-oxypyrimidine[2] (VIII) reacted abnormally. In the first case we obtained a mixture of the corresponding 1- and 3-benzyl derivatives, while with the second mercaptopyrimidine an inseparable mixture of the corresponding 1-benzyl-and 6-benzoxypyrimidines was obtained. The total yields of the alkylation products, in these two cases, were 94.0 and 87.5 per cent., respectively, of the calculated amounts.


(VII)

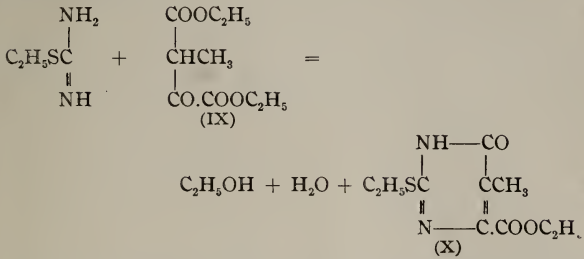

(VIII)

Therefore, in the case of methyl and ethylmercaptopyrimi dines of Type (I), the substitution of a methyl group in positions 4 or 5 and a bromine atom or a negative ethoxy group in position 5 of the pyrimidine ring does not favor the formation of 6-benzoxypyrimidines (IV). The specific aim of the work described in this paper was to investigate the action of benzyl chloride on a 2-mercaptopyrimidine of Type (I), in which both positions 4 and 5 are substituted, and determine whether a strongly negative group functionating in position 4 of the ring would favor the formation of an oxygen substitution product (imido ester).

The pyrimidine which we selected for our investigation was ethyl 2-ethylmercapto-5-methyl-6-oxypyrimidine-4-carboxylate (X). This is easily prepared by condensation of pseudoethylthiourea with diethyl oxalopropionate[3] (IX), and has already been described in a previous paper from this labora-

[1] Johnson and Jones: This Journal, **40**, 538.
[2] Wheeler and McFarland: *Ibid.*, **42**, 101.
[3] Arnold: Ann. Chem. (Liebig), **246**, 329, 336.

tory by Johnson and Mackenzie.[1] The condensation is represented as follows:

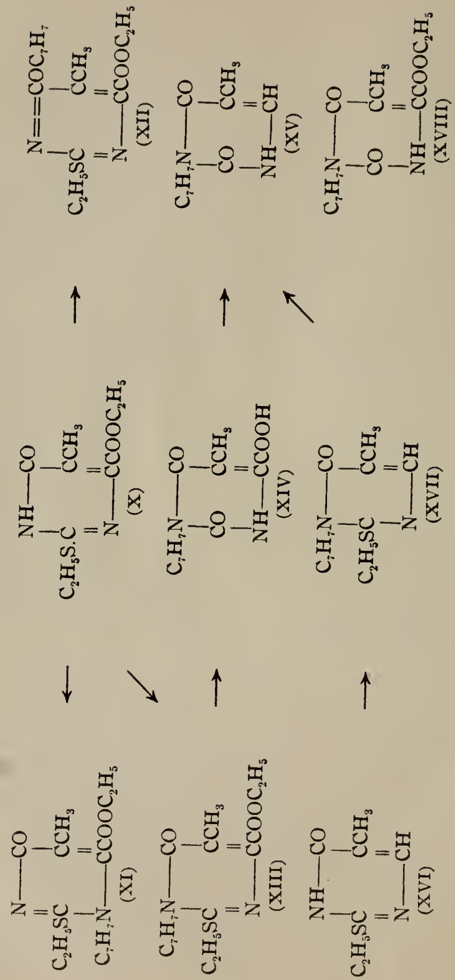


(IX) (X)

We now find that this pyrimidine (X) reacts smoothly with benzyl chloride in alcohol solution and in the presence of sodium ethylate, forming a benzyl derivative, in which the alkyl group is linked to the nitrogen occupying position 1 of the pyrimidine ring, viz., ethyl 1-benzyl-2-ethylmercapto-5-methyl-6-oxypyrimidine-4-carboxylate, represented by Formula (XIII). This pyrimidine is the chief product of the reaction; in fact, we were unable to isolate an isomeric 3-benzyl derivative in a pure condition. As regards a benzoxy derivative (XII), we obtained no evidence of its formation except the presence of a small amount of oil which contaminated the 1-benzylpyrimidine. Enough of this was, however, not obtained for further investigation.

That the product of our reaction was a 1-benzylpyrimidine (XIII) was established in the following manner: The mercapto compound, when digested with hydrochloric acid, underwent hydrolysis, with evolution of ethyl mercaptan and ethyl alcohol, forming quantitatively 1-benzyl-2,6-dioxy-5-methylpyrimidine-4-carboxylic acid (XIV). This acid was stable below its melting point, but when heated above this temperature (277°–279°) it underwent decomposition, with evolution of carbon dioxide, and was transformed smoothly into a benzylthymine melting at 203°–205°. This pyrimidine proved to be identical with 1-benzylthymine (XV), which

[1] This Journal, 42, 368.



Johnson and Derby[1] obtained by hydrolysis of 1-benzyl-2-ethylmercapto-5-methyl-6-oxypyrimidine (XVII) with hydrochloric acid. An attempt to prepare ethyl 1-benzyl-2,6-dioxy-5-methylpyrimidine-4-carboxylate (XVIII) by alkylation of ethyl 2,6-dioxy-5-methylpyrimidine-4-carboxylate[2] with benzyl chloride was unsuccessful. The ester simply underwent saponification, by action of the alkali, and the corresponding acid[3] was formed. These various changes are represented by the above structural formulas.

Ethyl 2-ethylmercapto-5-methyl-6-oxypyrimidine-4-carboxylate (X), therefore, reacts with benzyl chloride in the presence of alkali, and undergoes alkylation normally on a nitrogen atom, forming a 1-benzyl substitution product (XIII).

EXPERIMENTAL PART

Ethyl 2-Ethylmercapto-5-methyl-6-oxypyrimidine-4-carboxylate,

$$\begin{array}{lcl} NH & — & CO \\ | & & | \\ C_2H_5SC & & CCH_3 \\ \| & & \| \\ N & — & CCOOC_2H_5 \end{array}$$

.—This pyrimidine has been described in a previous paper from this laboratory.[4] It is obtained easily by condensation of pseudoethylthiourea with the sodium salt of diethyl oxalopropionate,

$$C_2H_5OOC.C(ONa) : C(CH_3)COOC_2H_5,$$

and crystallizes from alcohol in prismatic crystals which melt at 172°–173° to a clear oil.

Ethyl 2-Amino-5-methyl-6-oxypyrimidine-4-carboxylate,

$$\begin{array}{lcl} NH & — & CO \\ | & & | \\ H_2N.C & & CCH_3 \\ \| & & \| \\ N & — & CCOOC_2H_5 \end{array}$$

.—While the sodium salt of diethyl oxalopropionate condenses smoothly with either pseudomethyl- or pseudoethylthioureas, forming the corresponding mercaptopyrimidines, we were unable to obtain a good yield

[1] *Loc. cit.*
[2] Johnson: J. Biol. Chem., **3**, 299.
[3] Johnson: *Loc. cit.*
[4] Johnson and Mackenzie: This Journal, **42**, 368.

of the above pyrimidine by condensation of this salt with guanidine. The sodium salt was prepared, as directed in our previous paper, by condensing 71.0 grams of diethyl oxalate with 50.0 grams of ethyl propionate in the presence of 11.5 grams of finely divided sodium. The salt was then dissolved in water with 58.0 grams of guanidine sulphocyanide and the solution combined with a strong aqueous solution of sodium hydroxide (20 grams). After allowing to stand for about 48 hours the solution was then acidified with hydrochloric acid, when this aminopyrimidine separated as a pink powder. The yield was small. This substance was difficultly soluble in cold water but separated from a hot solution in prismatic crystals which had no definite melting point. A nitrogen determination gave (Kjeldahl):

	Calculated for $C_8H_{11}N_3O_3$	Found
N	21.26	21.03

Action of Benzyl Chloride on Ethyl 2-Ethylmercapto-5-methyl-6-oxypyrimidine-4-carboxylate

Ethyl 1-Benzyl-2-ethylmercapto-5-methyl-6-oxypyrimidine-4-carboxylate,

$$\begin{array}{lcl} & C_6H_5CH_2N & \text{---} \; CO \\ & | & \quad | \\ C_2H_5S.C & & \quad CCH_3 \\ & \| & \quad \| \\ & N & \text{---} \; CCOOC_2H_5 \end{array}$$

.—Four-tenths of a gram of sodium was dissolved in absolute alcohol, to which was then added 4.0 grams of ethyl 2-mercapto-5-methyl-6-oxypyrimidine-4-carboxylate and 2.1 grams of freshly distilled benzyl chloride. On warming sodium chloride began to separate at once and after heating a few hours (4–5 hours) on the steam bath the reaction was complete. The solution was then cooled, the sodium chloride separated by filtration and the alcohol filtrate concentrated to a small volume and then diluted with water. An oil deposited which solidified immediately after cooling. It was separated by filtration and dried on a porous plate to remove a trace of oily impurity which was present. The pyrimidine was extremely soluble in warm absolute alcohol and insoluble in

petroleum ether. It was purified by crystallization from alcohol and separated, on cooling, in colorless needles which melted at 69°–71° to a clear oil without effervescence. The yield of the purified pyrimidine was about 60.0 per cent. of the calculated. After concentration of the alcohol filtrates, more of the impure pyrimidine was obtained, but we were unable to isolate an isomeric benzyl derivative in pure condition. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{20}O_3N_2S$	Found
N	8.43	8.50

1-Benzyl-2,6-dioxy-5-methylpyrimidine-4-carboxylic Acid,

$C_6H_5CH_2N$——CO
|　　|
CO　CCH_3 .—A quantitative yield of this pyrimi-
|　　‖
NH——CCOOH

dine was obtained by hydrolysis of the preceding pyrimidine with strong hydrochloric acid. It was insoluble in water and alcohol, but could be purified easily by crystallization from glacial acetic acid. It separated from this solvent in hexagonal tables which melted at 277°–279° with violent effervescence. It did not respond to a test for sulphur. A nitrogen determination gave (Kjeldahl):

	Calculated for $C_{13}H_{12}O_4N_2$	Found
N	10.80	11.1

1-Benzyl-2,6-dioxy-5-methylpyrimidine (*1-Benzylthymine*)

$C_6H_5CH_2N$——CO
|　　|
CO　CCH_3.—The above 1-benzyl-2,6-dioxy-5-methyl-
|　　‖
NH——CH

pyrimidine-4-carboxylic acid was heated in a sulphuric acid bath at 285°–295° until effervescence ceased and all carbon dioxide was expelled. We obtained a dark oil, which solidified on cooling. This substance was then purified by crystallization from hot alcohol and separated, on cooling, in prismatic crystals which melted sharply at 203°–205° to a clear oil without effervescence. A mixture of this substance with

some 1-benzylthymine obtained in a previous investigation[1] melted at exactly the same temperature. Furthermore, the pyrimidine reacted with diazobenzenesulphonic acid, in the presence of sodium hydroxide, giving a characteristic purple solution. The yield was good. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{12}O_2N_2$	Found
N	12.96	12.9

An attempt to alkylate ethyl 2,6-dioxy-5-methylpyrimidine-4-carboxylate[2] with benzyl chloride in the presence of sodium ethylate was unsuccessful. One and five-tenths grams of the ester were digested in alcohol with the required amounts of sodium ethylate and benzyl chloride for 3 hours. The alcohol was then evaporated and the crystalline residue dissolved in water. On acidifying with hydrochloric acid we obtained 2,6-dioxy-5-methylpyrimidine-4-carboxylic acid,[2] which decomposed at about 325° with violent effervescence. The ester therefore simply underwent saponification by the above treatment and we obtained no evidence of the formation of a benzyl derivative. Analysis (Kjeldahl):

	Calculated for $C_6H_6O_4N_2$	Found
N	16.47	16.20

New Haven, Conn.
January, 13, 1913

ON THE PREPARATION AND PROPERTIES OF THE AMMONIUM SALTS OF SOME ORGANIC ACIDS[3]

By LeRoy McMaster

Most of the ammonium salts of organic acids described in the literature consist of a molecule of the ammonium salt combined with a molecule of the free acid in the case of monobasic acids, while, in the case of dibasic acids, the ammonium salt described is generally an acid ammonium salt. They were usually prepared by neutralizing an aqueouss solution of the acid with ammonia water or ammonium carbonate, and the

[1] Johnson and Derby: *Loc. cit.*
[2] Johnson: *Loc. cit.*
[3] Presented before the St. Louis Academy of Science, Feb. 17, 1913.

solution allowed to evaporate to crystallization. Many of the salts thus formed also contained water of crystallization.

In attempting to prepare some diammonium salts by the above method, Keiser and McMaster[1] always obtained the acid salts. They then dissolved the organic acids in absolute alcohol or ether and conducted into the solution a stream of dry ammonia gas. White crystalline salts were precipitated. In this manner they prepared the ammonium salts of fumaric, maleic, mesaconic and citraconic acids, which, upon analysis, proved to be the diammonium salts. Ammonium salts of malonic acid and *o*-phthalic acid were also prepared but were not analyzed.

I have continued this work on the dibasic acids, and have prepared the neutral ammonium salts of malonic, succinic, malic, tartaric, *o*-phthalic and *m*-phthalic acids. The method was applied also to the preparation of the ammonium salts of some monobasic acids—propionic, isobutyric, palmitic, benzoic and cinnamic. Some of the properties of these ammonium organic salts have also been studied. All of the acids used were obtained from Kahlbaum, except the tartaric acid, which was Baker's analyzed product.

Ammonium Malonate.—Finkelstein[2] attempted to make the neutral ammonium salt of malonic acid by adding an excess of ammonia water to an aqueous solution of the acid and allowing the mixture to evaporate over lime. The liquid lost ammonia and finally became acid. The acid ammonium salt crystallized out. I have prepared the neutral salt of malonic acid by the method described by Keiser and McMaster, but with some difficulty. If ammonia gas is conducted into an ethereal solution of the acid until no further precipitate is formed, the salt will be found not to be neutral. Analysis of two samples of the salt thus prepared gave respectively 16.65 per cent. and 16.62 per cent. of nitrogen. The acid ammonium salt of malonic acid contains 11.57 per cent. of nitrogen and the neutral salt 20.29 per cent. nitrogen. It is thus evident that each of these preparations was a mixture

[1] This Journal, **49**, 84.

[2] Finkelstein: Ann. Chem. (Liebig), **133**, 338.

of the acid ammonium salt and the neutral salt. In this experiment dry ammonia was conducted into an ethereal solution of 5 grams of malonic acid for about one-half hour. However, if the ammonia is run into a solution of 5 grams of malonic acid for about three hours and allowed to come in contact with the precipitated salt, the neutral ammonium malonate is formed. The salt thus prepared is a white crystalline powder, not deliquescent but readily soluble in water. The aqueous solution is neutral. The salt, on analysis, gave the following results:

	Calculated for $CH_2(CO_2NH_4)_2$	Found I	Found II
N	20.29	20.3	20.26

The first nitrogen determination was made by the Dumas method, the second by the Kjeldahl method.

Ammoniun Succinate.—Berzelius states in his *Lehrbuch der Chemie* that the salt which results from the evaporation of a neutral solution of ammonium succinate is an acid salt. By adding an excess of ammonia to a solution of succinic acid and allowing the liquid to evaporate, Doepping[1] obtained a salt that was easily soluble in alcohol and not deliquescent. He concluded that he had a neutral salt. Fehling[2] found that the neutral salt could not be so easily prepared, and that the salt obtained by the method of neutralization and evaporation is either an acid salt or a mixture of the acid and neutral salts, especially if ammonia is used in excess. He obtained the neutral ammonium salt by adding to basic lead acetate an excess of a solution of neutral ammonium succinate and evaporating in a vacuum over sulphuric acid the mother liquor. As soon as the mass was mostly crystallized out, it was washed with a little water to remove traces of lead, pressed between filter paper and dried at 40°–50°. Fehling thus obtained the neutral ammonium succinate in crystalline form.

Dry ammonia gas was run into an alcoholic solution of succinic acid, and a white crystalline powder was formed which was not deliquescent in the air but dissolved readily in water.

[1] Doepping: Ann. Chem. (Liebig), **47**, 253.
[2] Fehling: *Ibid.*, **49**, 154.

The aqueous solution was neutral to sensitive litmus paper. The salt is only very slightly soluble in alcohol and was washed on the filter with alcohol and ether. The salt can also be prepared by conducting the ammonia into an ethereal solution of succinic acid.

The salt prepared in absolute alcohol gave, on analysis, the following results:

	Calculated for $(CH_2CO_2NH_4)_2$	Found I	Found II
N	18.42	18.36	18.38

Prepared in ether:

N		18.38

Ammonium Malate.—No record can be found of the preparation of neutral ammonium malate. The acid malates have been made and extensively studied by Pasteur[1] and Bremer.[2] When ammonia gas is run into an alcoholic solution of malic acid, there is first formed a white mucilaginous substance which soon changes to a crystalline powder. Analysis proved this salt to be a mixture of ammonium acid malate and the neutral malate. The neutral salt was prepared by passing the gas into a solution of 5 grams of the acid for several hours, the salt filtered off by suction, washed with alcohol and ether, dried in a desiccator, and then placed in a dry flask, filled with ammonia and tightly stoppered. The flask was shaken at intervals, and portions taken out from time to time and tested for neutrality. It was found necessary to allow the salt, prepared as described above, to stand in contact with the ammonia for three days in order to become neutral. The compound thus prepared was very slightly deliquescent and dissolved readily in water.

Determinations of nitrogen by the Kjeldahl method gave:

	Calculated for $C_4H_4O_5(NH_4)_2$	Found I	Found II
N	16.66	16.64	16.63

Ammonium Tartrate.—Tartaric acid was dissolved in absolute alcohol and ammonia gas passed into the solution until

[1] Pasteur: Ann. Chem. (Liebig), **82**, 331.

[2] Bremer: Ber. d. chem. Ges., **13**, 352.

a portion of the salt on being dissolved in water showed a neutral solution. When the ammonia was first passed in a white curdy precipitate formed. This soon changed to an amorphous powder which, as soon as neutral, was filtered by suction on an alundum crucible and washed with alcohol and ether. The salt is not at all deliquescent, and is very slightly soluble in alcohol.

Analysis gave the following result:

	Calculated for $C_4H_4O_6(NH_4)_2$	Found
N	15.21	15.19

Ammonium o-*Phthalate.*—Marignac[1] describes the preparation of this salt by the action of liquid ammonia on the acid. This salt was precipitated from an alcoholic solution of *o*-phthalic acid by dry ammonia, filtered by suction on an alundum crucible, washed with alcohol and ether, and dried in a desiccator. It is a fine white powder, soluble in water, scarcely soluble in alcohol. The salt is not deliquescent.

	Calculated for $C_6H_4(CO_2NH_4)_2$	Found
N	14.00	13.98

Ammonium m-*Phthalate.*—On passing ammonia gas into an alcoholic solution of *m*-phthalic acid a very voluminous, white, gelatinous precipitate was formed, which changed to a white powder. The salt was filtered by suction, and washed with only a small amount of alcohol, as it is somewhat soluble in this medium in the absence of the ammonia. The complete precipitation of this salt in alcohol depends, therefore, upon an excess of ammonia. Ammonium *o*-phthalate, on the other hand, is quite insoluble in alcohol. It was impossible to prepare ammonium *p*-phthalate by this method on account of the insolubility of *p*-phthalic acid in both alcohol and ether.

The ammonium *m*-phthalate was dried in a desiccator, and, on analysis, gave:

	Calculated for $C_6H_4(CO_2NH_4)_2$	Found
N	14.00	13.96

[1] Marignac: Ann. Chem. (Liebig), **42**, 215.

The method having proved so very applicable in the preparation of neutral ammonium salts of dibasic acids, it was next tried on the preparation of neutral ammonium salts of monobasic acids. Some work is in progress in this laboratory on the preparation of neutral salts of tribasic acids by the same method.

Ammonium Propionate.—When ammonia gas was first passed into an ethereal solution of propionic acid, no precipitate formed. White fumes came off which condensed in the top of the flask to a beautiful snow-white substance. After the gas was passed in for a short time, a white voluminous precipitate formed. The precipitate was quickly filtered by suction, washed with ether, placed in a vacuum desiccator for a few minutes and then in a calcium chloride desiccator. The salt deliquesces very readily, and is very soluble in water. On first dissolving the salt in water, the solution is neutral. The solution, however, soon turns acid, due to hydrolysis. The salt is very soluble in methyl alcohol, ethyl alcohol and acetic acid. Analysis proved it to be the neutral ammonium propionate.

	Calculated for $C_2H_5CO_2NH_4$	Found
N	15.38	15.4

Ammonium Isobutyrate.—Isobutyric acid was dissolved in ether, and ammonia passed into the solution. A snow-white precipitate of lustrous appearance formed. This was filtered by suction, washed with ether, and dried in a desiccator. Though not deliquescent, the salt cannot be dried in the air for it has a very high vapor tension. An appreciable quantity of the salt will disappear entirely in a short time if exposed to the air. The salt is soluble in alcohol and water. The aqueous solution is neutral.

Determination of nitrogen by the Kjeldahl method gave:

	Calculated for $C_4H_7O_2NH_4$	Found
N	13.33	13.32

Ammonium Benzoate.—By evaporating a solution of benzoic acid neutralized with ammonia there is obtained an acid salt

of the formula $NH_4C_7H_5O_2.C_7H_6O_2$ (Berzelius). The neutral salt can be obtained by conducting ammonia gas into an ethereal solution of benzoic acid. A white gelatinous precipitate was formed, which, after being filtered and washed with ether, dried in the air to an amorphous powder. It is not deliquescent, but soluble in water in which it shows a neutral reaction. The salt is somewhat soluble in ethyl alcohol, from which it can be crystallized. Analysis proved it to be the neutral ammonium benzoate.

	Calculated for $C_6H_5CO_2NH_4$	Found
N	11.02	11.02

Ammonium Cinnamate.—When ammonia gas was passed into an ethereal solution of cinnamic acid a white gelatinous precipitate at first formed which turned to an amorphous powder. It was necessary to pass the gas into the solution for several hours in order to obtain the neutral salt. The salt is soluble in water, and is not deliquescent in the air. If the salt is crystallized from alcohol, beautiful white crystals are formed which have a marked odor of oil of cinnamon. The original salt prepared in ether has no such odor. Also, the salt crystallized from alcohol is very much less soluble in water than the original salt. Ammonia was passed into an alcoholic solution of cinnamic acid, and there were formed at once glistening white crystals. After the ammonia was passed into the solution for some time, the alcohol was poured off from the crystals into a crystallizing dish and allowed to evaporate spontaneously. A further quantity of the crystals was obtained. These crystals, prepared from the alcoholic solution of the acid, had an odor of oil of cinnamon, but not so marked as in the case of the salt prepared in ethereal solution and afterwards crystallized from alcohol. The crystals prepared in alcohol were again found to be much less soluble in water than the amorphous powder prepared in ether.

Determination of nitrogen in the salt prepared in ether gave the result:

	Calculated for $C_9H_7O_2NH_4$	Found
N	8.48	8.49

Action of Ammonia on Palmitic Acid.—When dry ammonia gas was passed into an ethereal solution of palmitic acid there was produced at once a very voluminous, white gelatinous precipitate. The precipitate did not become crystalline even after passing in the gas for three hours. The precipitate was filtered by suction and washed with ether. It dried in the air to a white substance resembling a "soap." It was soluble in alcohol, especially if the alcohol was warm. Ammonia was also passed into an alcoholic solution of palmitic acid for three hours. No precipitate formed at first, but as the ammonia gas continued to pass into the solution a precipitate was formed which after a while dissolved and again after a short time reprecipitated. The precipitate and alcoholic solution were poured into a crystallizing dish and the alcohol allowed to evaporate. While wet with alcohol the precipitate was granular in appearance, but after the alcohol had entirely evaporated and the compound became dry, it had the appearance of the compound prepared in ether. The compound prepared in each case was evidently an ammonium "soap." It was not analyzed.

This investigation is being continued with other organic acids.

WASHINGTON UNIVERSITY
ST. LOUIS, MO.
Feb. 18, 1913

REPORTS

KETO-ENOL TAUTOMERISM

Quantitative Determination of Keto-Enol Tautomers

Until very recently, practically all quantitative determinations of the components of keto-enol tautomeric mixtures have been based on physical methods which, to be sure, are capable of great accuracy but the interpretation of which is generally uncertain. Of the chemical methods, that of Wislicenus,[1] based on the coloration of ferric chloride solutions produced by enol compounds, is limited to substances which rearrange very slowly, as ferric chloride not only disturbs the equilibrium but also increases catalytically the rearrangement velocity.

[1] Ann. Chem. (Liebig), **291**, 178 (1896). For a recent application of this method, see Knorr and Schubert: Ber. d. chem. Ges., **44**, 2772 (1911).

Claisen's method, depending on the solubility of enol compounds in dilute sodium carbonate solutions, can be applied only to substances in the solid state. The method proposed by Michael and Smith,[1] based on the action of tertiary bases, gives entirely erroneous results.

Of the physical methods, that based on the behavior towards electrical waves, which are absorbed only by hydroxyl compounds, is likewise unreliable.[2] The results obtained by the molecular rotation,[3] molecular refraction[4] and absorption methods[5] are trustworthy; the last method, which should prove especially valuable with substances which rearrange quickly, is limited, however, to solutions and in solvents which do not absorb light in the ultraviolet.

Kurt H. Meyer, of the Munich Academy of Sciences, has recently worked out a method which is extremely simple in operation, is applicable to either solids, liquids or solutions in any solvent and is apparently very accurate. By means of this method he has been able to make a large and very important contribution to our knowledge of keto-enol tautomeric compounds. The results of his investigation are published in a series of papers[6] which appeared during 1911 and 1912.

The method is based on the fact that all enols, which, of course, also contain a double bond, react instantly with bromine while all compounds which are unquestionably ketones do not. This difference is most marked in alcohol. In its simplest form, the determination is carried out as follows: The substance to be tested is quickly dissolved in alcohol and at once titrated with a standard solution of bromine in alcohol until the color of the bromine just persists after shaking. The reaction probably consists in the addition of bromine to the enol, RR′C : C(OH)R″, with formation of an unstable dibromide, RR′CBrC(OH)BrR″, which quickly loses hydrobromic acid, yielding a bromo ketone, RR′CBrC(: O)R″. Alcoholic solutions of bromine, however, are not stable and must be restandardized every time before using. Now the bromo ketones formed in the reaction are quantitatively reduced by hydriodic acid, on gentle warming in alcohol, to the ketone, with liberation of iodine which can be titrated with thiosulphate. Hydriodic acid probably adds to the bromo ketone,

[1] Ann. Chem. (Liebig), **363**, 36 (1908).

[2] Drude: Ber. d. chem. Ges., **30**, 940 (1897).

[3] Perkin: J. Chem. Soc., **61**, 800 (1892).

[4] Brühl: J. prakt. Chem., **50**, 119 (1894). See also Auwers: Ber. d. chem. Ges., **44**, 3525 (1911).

[5] Hantzsch: Ber. d. chem. Ges., **43**, 3049 (1910); **44**, 1771 (1911).

[6] Ann. Chem. (Liebig), **380**, 212, 220 (1911). Ber. d. chem. Ges., **44**, 2718, 2725, 2729 (1911); **45**, 2843, 2864 (1912).

while the bromine is replaced by iodine, a compound of the type RR'ClC(OH)IR" being formed; such compounds, as shown by Finkelstein,[1] liberate iodine spontaneously:

$$RR'ClC(OH)IR'' \longrightarrow RR'C:C(OH)R'' + I_2$$

The substance to be tested, quickly dissolved in 50 cc. of 96 per cent. alcohol at about 10°, is treated at once with an approximately 0.1 N solution of bromine in alcohol (its exact concentration need not be known) in 0.5 cc. portions at a time and shaken after each addition until the color of the bromine persists about 2 seconds; the bromine is then decolorized with a few drops of thiosulphate solution, 5 cc. of a 5 per cent. solution of potassium iodide solution added, the mixture warmed gently and the iodine titrated to permanent decolorization with thiosulphate. It is best to prepare fresh bromine solutions before every determination, as old solutions influence the results of the titrations, probably owing to the formation of bromoacetaldehyde, which liberates iodine from hydriodic acid. The accuracy of the method may be judged from the following results obtained with artificially prepared mixtures of the pure enol and keto forms of acetyldibenzoylmethane:

Per cent. enol taken	100.0	45.5	28.04	37.85	25.0	68.70
Per cent. enol found	99.8	43.5	28.96	39.8	27.0	71.30

The addition of carbon tetrachloride or chloroform makes the end point somewhat less sharp, but does not influence the results. A large excess of alcohol must be present, however, and it is better, therefore, to use alcoholic solutions of bromine rather than the more stable chloroform solutions. If the ketone and enol are allowed to stand in alcohol, they will, of course, rearrange until equilibrium is established. After 12 hours, a 0.2 N solution of the originally pure ketone was found to contain 74.0 per cent. enol, that of the originally pure enol only 75.5 per cent., i. e., the same equilibrium point was reached, as was expected, from either the pure ketone or the pure enol side.

Tautomerism of Acetoacetic Ester

As this method of determination can be carried out very quickly, it seemed that it ought to be applicable to substances consisting of mixtures of labile tautomers, and Meyer undertook the investigation, by its means, of the ever-interesting problem of acetoacetic ester.

Solutions of the liquid ester in alcohol at —7°, titrated as described above, gave, as the result of determinations on 5

[1] Ber. d. chem. Ges., **43**, 1528 (1910).

solutions of different concentrations, 7.71, 7.71, 7.72, 7.70 and 7.75 per cent. enol. As the titration requires only 20-25 seconds, the error due to enolization during the determination is very slight; a solution allowed to stand 25 seconds after the end point had been reached absorbed about 0.2 cc. more of the bromine solution for each gram of ester. This error can be obviated by decolorizing the bromine with thiosulphate as soon as the end point is reached, adding 1–2 drops more of the thiosulphate, then the potassium iodide, and titrating back as before.

Experiments in solvents other than ethyl alcohol, viz., methyl, propyl and amyl alcohols, chloroform and water, gave the mean value 7.71 for the percentage of enol in the ordinary liquid ester. This value is thus seen to be independent of the nature of the solvent and of the concentration.

By applying the above method to solutions which have stood varying lengths of time, both the velocity of rearrangement and the equilibrium point can, of course, be determined. In solvents like hexane and carbon disulphide, the enol cannot be titrated directly, as the ester undergoes further bromination without a color change when the enol is used up; this difficulty can be obviated by diluting the solutions with a large volume of cold alcohol and titrating quickly. Below are given the percentages of enol at equilibrium in various solvents, together with the dielectric constants and association factors of the solvents:

Solvent	Per cent. enol	Dielec. const.	Assn. factor
Water	0.4	81.1	3.8
Glacial acetic acid	5.74	6.5	3.62
Methyl alcohol	6.87	35.4	3.43
Acetone	7.3	20.7	1.26
Liquid ester	7.71	....	....
Chloroform	8.2	5.2	....
Nitrobenzene	10.1	34.0	0.93
Ethyl alcohol	12.0	26.3	2.74
Ethyl acetate	12.9	6.1	
Benzene	16.2	2.25	
Ether	27.1	4.6	
Carbon disulphide	32.4	2.6	
Hexane	46.4	1.85	

As shown by the table, there is no relation between the amount of enol and the two series of constants for the solvents.

In *solution*, the amount of keto form increases with rise in temperature; thus, boiling solutions of the ester in methyl

and ethyl alcohol, when poured into much alcohol at $-7°$ and titrated, gave only 4.74 and 7.50 per cent. enol, respectively. Heating the liquid ester alone, however, does not perceptibly change the equilibrium point, but distillation increases the amount of enol to 20–25 per cent.

Since the ratio of the concentrations, C_k/C_e, of the two forms at equilibrium in any given solvent is equal to the ratio of their solubilities, S_k/S_e, in that solvent, multiplied by some constant, K, independent of the solvent,[1] and since in a water solution of acetoacetic ester only 0.4 per cent. is present as enol, it seemed probable that the latter form would be much less soluble in water than the keto form. As a matter of fact, if a cold alkaline solution of the ester is acidified, an oil is precipitated which at once gives an intense color with ferric chloride and immediately decolorizes bromine. This oil is the free enol form but quickly rearranges into the keto form and redissolves. This isomerization is so rapid that a titration of the oil showed only 50 per cent. enol. Since in water the ester is present almost entirely as ketone, the solubility of the keto form may be taken as equal to that of the ordinary ester in that solvent (11.6 grams in 100 grams of solution at 0°). For the sake of comparison with the enol form, the solubility of the ordinary ester in 2 per cent. sodium chloride solution was also determined (10.9 grams in 100 grams solution). Again, since the enol form is precipitated from alkaline solutions by acids, its solubility in dilute sodium chloride solution can be approximately determined by preparing solutions of the ester of varying concentrations in dilute sodium hydroxide and noting which solution just becomes turbid on acidification with hydrochloric acid. In this way it was found that 0.5 gram of the enol dissolves in 100 grams of 2 per cent. sodium chloride solution. Knowing C_k, C_e, S_k and S_e, the constant K in the van't Hoff-Dimroth equation can be calculated. It comes out 0.09. In hexane, therefore, in which the ester, at equilibrium, contains 46 per cent. enol, the enol should be 9 times more soluble than the ketone form, and, as a matter of fact, by shaking the liquid ester with hexane, practically all the enol can be removed, leaving the almost pure ketone (98.5 per cent.).

Investigation of the rearrangement velocity of the ester by the bromine titration method gave the following values for the ketonization (K_k) and enolization (K_e) constants, respectively, at 0°:

[1] See Dimroth: Ann. Chem. (Liebig), **377**, 127 (1910).

Solvent	K_k	K_e
Liquid ester	0.00055	0.000046
Water	2.4	0.010
Alcohol (99.8 per cent.)	0.077	0.0105
Hexane	0.0041	0.0035

By Lapworth's method[1] (determination of the time required by the keto form to decolorize varying amounts of bromine), the value 0.013 was obtained for K_e in water at 0° and 0.039 at 10°. The somewhat higher value for 0°, as compared with that obtained by Meyer's method, is due to the fact that the hydrobromic acid formed in the Lapworth reaction catalyzes the rearrangement. Impurities, indeed, have marked catalytic effects, varying in magnitude with the nature of the solvent. In water and alcohol they are not so pronounced; the value for K_e in 0.1 N hydrochloric acid at 0° is 0.018. In nondissociating solvents, the influence of halogen acids is enormous; a few seconds after dissolving the ester in hexane or carbon disulphide containing hydrobromic acid, the percentages of enol were found to be 44.4–46.1 and 33.4, respectively. This probably explains why sharp end points in the bromine titration method are not obtained in these solvents, as hydrobromic acid is liberated in the reaction between the bromine and the enol. This catalytic effect of acids is apparently not due to hydrogen ions, since it is less marked in dissociating solvents. It is probably purely chemical, the acid adding to the ketone and then splitting off.

A short time after the appearance of Meyer's first two papers, Knorr, Rothe and Averbeck[2] published the results of an investigation in which they also succeeded in separating the two forms of the ester. They found that at the temperature of a carbon dioxide-ether mixture (—78°) the reversible transformation of the two forms of the ester into each other practically comes to a standstill and that the keto form is difficultly soluble in most solvents and can be crystallized from solvents which do not freeze at this temperature (alcohol, ether, hexane, ligroin, etc.) by cooling sufficiently concentrated solutions to —78°. In this way they obtained the keto form from ether or ether-alcohol mixtures in needles often 1–2 cm. long which, in a specially constructed apparatus from which all moisture was excluded, could be washed entirely free of the mother liquors containing the enol by means of low boiling (20°) ligroin or methyl ether. On drying in a high vacuum at —78°, the keto ester is obtained in perfectly pure condi-

[1] J. Chem. Soc., **85**, 30 (1904).

[2] Ber. d. chem. Ges., **44**, 1138 (1911).

tion. At —78° or in liquid air it is stable for a long time, and even at room temperature it requires weeks and months to reach the equilibrium point of the ordinary ester if catalytic influences are carefully excluded. In small quantities the ester can even be distilled in a vacuum without marked change. It boils at 40°–41° under 2 mm., solidifies sharply at —39° and its refractive index at 10° for the line *D* is 1.4225. It thus differs but slightly from the ordinary ester, which boils at 39°–40°, solidifies indefinitely at —45° to —43° and has the refractive index 1.4230–1.4232. At *room temperature*, according to the authors, it shows the same behavior towards ferric chloride as does the ordinary ester, but if equal amounts of the keto ester and the ordinary equilibrium mixture in various solvents at —78° are treated with equal amounts of ferric chloride in ether at —78° and then warmed up to —40° in the course of 2 minutes, markedly different periods of time are required for the appearance of the first faint red coloration, as shown in the following table:

Solvent	Equil. mixt.	Keto ester
Ether	Immediately	1 min. 20 sec.
Butyl alcohol	0 min. 6 sec.	....
Propyl alcohol	0 min. 8 sec.	2 min. 0 sec.
Ethyl alcohol	0 min. 14 sec.	1 min. 20 sec.
Methyl alcohol	1 min. 20 sec.	1 min. 30 sec.

At —78° in alcohol, the reaction with the equilibrium mixture is perceptible in about 10 minutes, with the keto ester in only about 1.5 hours.

The isolation of the pure enol ester presented more difficulties. The sodium salt of the ester was treated, in small portions in suspension in petroleum ether (boiling below 20°) or methyl ether, with *not quite* the amount of hydrochloric acid gas necessary for complete decomposition of the salt, the sodium chloride filtered off, and the solution concentrated as quickly as possible at —78°, moisture being very carefully excluded. A specially constructed form of apparatus was used for these operations. The enol ester thus obtained is a colorless oil of strong, pleasant, fruity odor, solidifying in liquid air to a glassy mass which soon becomes crystalline. In very small quantities and in a very high vacuum, it can be distilled at about 33° without much change. Its refractive index at 10° for the line *D* is 1.4480. In ether-alcohol at —50°, it begins to show a red color with ferric chloride solution in 30–45 seconds, while the keto form under the same conditions requires 6 minutes 20 seconds.

By making artificial mixtures of the two pure forms and determining their refractive indices, a curve was constructed by means of which the composition of any mixture, and hence the composition at equilibrium and the velocity of rearrangement, could be determined. With the Abbé refractometer, only two drops of liquid are necessary for a determination. Using this method, the authors found that the ordinary equilibrium mixture of ester contains 2 per cent. enol, whereas Meyer, as shown above, obtained 7.71 per cent. Temperature does not appreciably affect the equilibrium. For the ketonization and enolization constants of the ordinary ester, they found 0.000172 and 0.00000376, respectively. The nature of the glass walls in which the determination is made has an enormous influence; the above values were obtained in a vessel which had been treated with hydrochloric acid, while in a new apparatus a value 100 times as large, viz., 0.0178, was obtained for $K_k + K_e$. Again, for a freshly distilled preparation of the enol ester, a still larger value, 0.613, for $K_k + K_e$ was found. Traces of both acids and bases, such as hydrochloric acid or tripropylamine fumes, cigarette smoke, contact with soft glass containing alkali, etc., exert a powerful catalytic influence on the ketonization. The authors observed that the percentage of enol in freshly distilled samples of the ordinary ester varies with the conditions of the distillation, the rapidity with which the hot vapors are condensed, etc. They also determined the percentage of enol at equilibrium in various solvents by concentrating the solutions at —78° and determining the refractive indices of the residues. They obtained the following values: In ether, 11 per cent. enol; in carbon disulphide, 25; in chloroform, 2; in petroleum ether, 27.5; in hexane, 31. These results, as will be seen, differ considerably from those obtained by Meyer.

Thus, although qualitatively Knorr's results agree with Meyer's, there are marked quantitative differences. The latter accordingly reinvestigated his method with a view to increasing its accuracy. In its simple form, it is subject to the following sources of error: The difficulty in determining the end point in the bromine titration; the rearrangement which may take place during the titration; the possibility that the alcoholic bromine solution may contain substances which liberate iodine from potassium iodide; and the possibility that the bromo ester formed may itself quickly react further with the bromine. The first two of these sources of error, which are the most serious, can be obviated by adding an excess of bromine and at once removing the excess. For this purpose a reagent must be used which reacts very rapidly with bro-

mine and not at all with iodine and whose reaction product with bromine is not affected by hydriodic acid. Such a substance is β-naphthol. Determinations by the modified method are carried out as follows: From 1–1.5 grams of the ester are quickly dissolved in 30 cc. of alcohol at —7°, enough 0.2–0.1 N alcoholic bromine solution to produce a yellow to brown color added at once, the mixture shaken and immediately treated with 2 cc. of a 10 per cent. β-naphthol solution until the bromine is decolorized. The whole operation requires but 15 seconds. Potassium iodide is now added and the solution is warmed and titrated with thiosulphate. As the mean of 7 determinations, the percentage of enol was found to be 7.51, with a maximum possible error due to isomerization during titration of 0.1–0.2 per cent. The true value may safely be taken as 7.4.[1] All the work reported in the earlier papers is likewise but slightly altered by the use of the modified method.

Applying his method to solutions increasing in dilution up to 0.2–0.1 N, Meyer made the surprising observation that the percentage of enol at equilibrium increases with the dilution, i. e., the equilibrium is not independent of the concentration. Below are given the results for the two extreme concentrations studied. The solutions were allowed to stand 3–4 days at room temperature in order to attain equilibrium. According to Meyer, the probable explanation is that even in the most dilute solutions studied the solvent is not "constant," i. e., it is not pure alcohol, benzene, etc., but a varying mixture of ester with alcohol, benzene, etc.:

Solvent	Conc. ester Per cent.	Per cent. Enol
Alcohol	65.0	7.8
Alcohol	1.0	13.2
Benzene	80.0	8.3
Benzene	2.1	20.6
Carbon disulphide	82.0	8.0
Carbon disulphide	0.9	39.2
Hexane	90.0	9.3
Hexane	1.7	58.6

The Ferric Chloride Reaction of Enols[2]

Just as the enol form of the ester can be determined by

[1] Auwers [Ber. d. chem. Ges., **44**, 3530 (1911)] recently obtained the value 9 per cent. by the refraction method.

[2] See Wislicenus: Ann. Chem. (Liebig), **291**, 172 (1896). Ber. d. chem. Ges., **32**, 2837 (1899). Hantzsch and Desch: Ann. Chem. (Liebig), **323**, 1 (1902). Stobbe: *Ibid.*, **352**, 132 (1907). Federlin: *Ibid.*, **356**, 251 (1907). Hantzsch: Ber. d. chem. Ges., **43**, 3068 (1910). Meyer: *Ibid.*, **44**, 2725 (1911). Knorr and Schubert: *Ibid.*, **44**, 2772 (1911).

titrating with bromine until the color of the bromine persists, so it can be determined in water in the presence of ferric chloride by adding bromine water quickly at 0° until the violet color of the iron enolate disappears. Experiments carried out in this way by Meyer showed that ferric chloride has an enolizing influence. The amount of enol at equilibrium depends upon the concentration of the ferric chloride but is not proportional to it. Probably part of the enol forms a complex with the ferric chloride and is not involved in the establishment of the equilibrium. In alcoholic solutions it is much more difficult to determine the amount of enolate formed on account of the indefiniteness of the end point and the great catalytic influence, in this solvent, of the ferric chloride on the rearrangement velocity. As is well known, the formation of the iron enolate is a slow process; by adding varying amounts of ferric chloride to an aqueous solution of the ester at 0° and determining the amount of enol formed after 5 minutes, Meyer found that the velocity of its formation is practically independent of the concentration of the ferric chloride. He concludes, therefore, that the formation of the enolate from the enol and ferric chloride is instantaneous and that the slow appearance of the color is due to the slow enolization of the keto form. In harmony with this view is the fact that if equal amounts of ester and ferric chloride are taken, the velocity curve obtained agrees well with that for a monomolecular reaction; the constant is 0.017, or approximately equal to that obtained for the rearrangement of the ester in 0.1 N hydrochloric acid, so that the catalytic effect of ferric chloride in water is about the same as that of free hydrochloric acid. As pointed out above, this catalytic influence is a serious objection to the use of the ferric chloride colorimetric methods for the determination of enols.

Desmotropy of Methyl Benzoylbenzoate

Meyer[1] and Knorr[2] simultaneously isolated the enol form of this ester. Both describe it as melting around 40° and Knorr gives the refractive index at 12°.5 for the line *D* as 1.5620, while that of the ordinary equilibrium mixture is 1.5418. Meyer finds by the bromine method that at equilibrium at room temperature the ordinary ester contains 16.7 per cent. enol; in glacial acetic acid at 20°, 14 per cent.; in alcohol, 21 per cent.; in carbon disulphide, 56 per cent.; in hexane, 69 per cent. The ketonization constant at 0° in alcohol is 0.10, the enolization constant 0.04. In boiling alcohol, the percentage

[1] Ber. d. chem. Ges., **44**, 2729 (1911).
[2] *Ibid.*, **44**, 2767 (1911).

of enol at equilibrium is 13.6. Unlike acetoacetic ester, however, the equilibrium point of methyl benzoylacetate is changed when the ester is heated without solvents; the percentage of enol decreases from 16.7 at 18° to 15.2 at 100° and 13.8–14.1 at 200°.

Relation between Constitution and Equilibrium in Keto-Enol Desmotropic Compounds

Having perfected his analytical method, Meyer now undertook a systematic study of a very large number of tautomeric keto-enol compounds. In this investigation he has made the following observations:

Homogeneously crystallized compounds are always homogeneous; equilibrium between keto-enol desmotropes never occurs in the crystalline state, only in the liquid and gaseous states and in solutions. No prediction can be made, from the structure of a solid, what its condition will be in solution. Thus, acetyldibenzoylmethane, which, in the solid state, has the keto form, is 90 per cent. enolized in alcohol, while the solid crystalline enolic methyl oxaloacetate is strongly ketonized in solution. This is brought out clearly in the following table:

Substance	Per cent. enol in cryst. solid	Per cent. enol at equil. in alcohol
Benzoylacetone	98	94
Dibenzoylmethane	96	90–100
β-Acetyldibenzoylmethane	2	90
Oxaloacetic acid	100	60
Benzoylacetic acid	98	40
Methyl oxaloacetate	100	23
Acetoacetanilide	1	18
Methylcyclohexanolonedicarboxylic ester	0	..

The percentages of enol at equilibrium in different tautomeric substances bear approximately the same ratio to each other in all solvents; in other words, if the percentages of enol in two substances are known in one solvent, the percentage of enol in one of them in any other solvent can be approximately calculated from the value for the other substance in that solvent. The following table gives the ratio *enol : ketone* of three tautomeric substances in various solvents. As this table shows, the relative amounts of enol in acetylacetone are, in all solvents, 30–50 times greater and those in methyl benzoylacetate about 2.2 times greater than in acetoacetic ester:

Solvent	Acetoacetic ester	Methyl benzoyl-acetate	Acetyl-acetone
Water	0.004	0.008	0.24
Formic acid	0.011	0.028	0.9
Glacial acetic acid	0.061	0.16	2.8
Methyl alcohol	0.074	0.16	2.6
Liquid tautomers	0.079	0.20	3.2
Chloroform	0.089	0.19	3.8
Ethyl alcohol	0.15	0.35	5.3
Benzene	0.22	0.45	5.7
Hexane	0.9	2.2	12.0

Compounds with One C(: O)R Group.—Such substances as acetaldehyde, acetone, acetophenone and pyroracemic acid contain no enol, even in alcoholic solution in the presence of sodium ethylate.

Compounds with Two C(: O)R Groups.—If, in compounds of this type, $R(O:)CCH_2C(:O)R'$, $R(O:)CCH_2$ is kept the same and $C(:O)R'$ is varied, it is found that the percentage of enol at equilibrium increases in the order $C(:O)R' = COOCH_3$, $COOC_2H_5$, COOH, $CONHC_6H_5$, $CO.CH_3$, $CO.C_6H_5$, COCOOR″, as shown by the following table:

Substance	Per cent. enol in Liquid tautomer	Per cent. enol in Alcohol
$H_3COOCCH_2$ combined with:		
$COOCH_3$	0	0
$CO.CH_3$	4.8	12.6
$CO.C_6H_5$	16.7	26.0
$COCOOCH_3$	100.0 (solid)	23.0(?)
$H_5C_2OOCCH_2$ combined with:		
$COOC_2H_5$	0	0
$CO.CH_3$	7.4	13.0
$CO.C_6H_5$	29.2	27.0
$COCOOC_2H_5$	88.0	50.0
$HOOCCH_2$ combined with:		
COOH	0	0
$CO.C_6H_5$	100.0 (solid)	40.0
COCOOH	100.0 (solid)	60.0
$H_3C.OCCH_2$ combined with:		
$COOCH_3$	4.8	12.6
$COOC_2H_5$	7.4	13.0
$CONHC_6H_5$	0 (solid)	18.0
$CO.CH_3$	76.0	84.0
$CO.C_6H_5$	100.0 (solid)	94.0

$H_5C_6.OCCH_2$ combined with:		
$COOCH_3$	16.7	26.0
$COOC_2H_5$	29.2	27.0
COOH	100.0 (solid)	40.0
$CO.CH_3$	100.0 (solid)	94.0
$CO.C_6H_5$	100.0 (solid)	90–100
$R''OOCCOCH_2$ combined with:		
$COOCH_3$	100.0 (solid)	23.0
$COOC_2H_5$	88.0	50.0
COOH	100.0 (solid)	60.0

The enolizing tendency of the group C(: O)H, i. e., R′ = H, was studied in only one case., viz., that of formylphenylacetic ester, $H_5C_2OOCCH_2C(: O)H$, which contains about 76 per cent. enol in the liquid state and 20–25 per cent. in alcohol.

If the acids, HOC(: O)R′, from which are derived the groups C(: O)R′, whose enolizing tendency has been determined as above, are arranged in order of increasing dissociation constants, as shown below, it will be seen that they fall into the same order as their derived groups arranged in order of increasing enolizing tendency.

Acid		Dissoc. const. $K = 100k$
$HOCOOCH_3$	Monomethyl carbonate	. . . . .
HOCOOH	Carbonic	0.00001
$HOCO.CH_3$	Acetic	0.0018
$HOCO.C_6H_5$	Benzoic	0.007
HOCO.H	Formic	0.021
HOCOCOOH	Oxalic	About 10.0

see errata p. 548

Compounds with Three Substituents.—No general relation can be established between the constitution of compounds of this type, R(O :)CCHR″C(: O)R′, and the percentage of enol they contain at equilibrium. When R″ is an alkyl the enol content is generally lower than when R″ is a hydrogen atom. If R″ is an acyl group, however, the enolization is generally increased if the unsubstituted compound itself is only slightly enolized; otherwise it is decreased. The results with this class of compounds are summarized below:

Substance $R'' = H$	Per cent. enol in liquid
$CH_3COCH_2COOCH_3$	4.8
$CH_3COCH_2COOC_2H_5$	7.4
$C_6H_5COCH_2COOC_2H_5$	29.2
$CH_3COCH_2COCH_3$	76.0
$H_5C_2OOCCH_2COOC_2H_5$	0
$CH_3COCH_2COOC_2H_5$	7.4
$C_6H_5COCH_2COCH_3$	enol stable

Substance	Per cent. enol in liquid
$R'' = $ alkyl	
$CH_3COCH(CH_3)COOCH_3$	3.0
$CH_3COCH(C_2H_5)COOC_2H_5$	3.1
$CH_3COCH(CH_2C_6H_5)COOC_2H_5$	5.0
$CH_3COCH(CH_2COOC_2H_5)COOC_2H_5$	3.7
$C_6H_5COCH(CH_2COOC_2H_5)COOC_2H_5$	4.1
$CH_3COCH(CH_3)COCH_3$	30.0
$R'' = $ acyl	
$H_5C_2OOCCH(COOC_2H_5)COOC_2H_5$	0.2
$H_5C_2OOCCH(COCH_3)COOC_2H_5$	64.0
$CH_3COCH(COCH_3)COOC_2H_5$	90–100
$CH_3COCH(COC_6H_5)COOC_2H_5$	60.0
$C_6H_5COCH(COOC_2H_5)COCH_3$	60.0
$C_6H_5COCH(COC_6H_5)COCH_3$	ketone stable

Desmotropy of Malonic Ester and Methanetricarboxylic Ester

Free malonic ester contains at most 0.01 per cent. enol, but if a solution in methyl alcoholic sodium methylate is poured directly into a strongly cooled, acidified solution of bromine in methyl alcohol so that the enol can be brominated at the instant that it is formed, as much as 50 per cent. enol can be detected.

Crystalline methanetricarboxylic ester is pure ketone; the liquid ester contains 0.2 per cent. enol; when liberated from its sodium methylate solution as described above for the malonic ester, 75–87 per cent. enol can be detected.

By these experiments Meyer has shown that ester groups can exhibit desmotropy just as well as ketone groups:

$$CHCOOR \rightleftarrows C : C(OH)R$$

C. A. R.

MOLECULARLY ASYMMETRIC METALLIC COMPOUNDS[1]

Gentlemen, permit me, first, to extend my sincere thanks to your President for the honor which he has done me in inviting me to lay before you the results of our investigations on molecularly asymmetric metallic compounds. These studies may be considered as a continuation of the investigations begun by one of your most famous countrymen, by Pasteur, and I could not better begin my report than by expressing the great satisfaction I feel in having been able to widen, to a

[1] Address by Prof. A. Werner, of the University of Zurich, delivered before the Chemical Society of France on May 24, 1912, and published in the Bull. soc. chim., for July 20, 1912.

small extent, the field of the application of his great principle of molecular asymmetry and to continue the work of Le Bel and van't Hoff.

Gentlemen, the hypotheses on the arrangement in space of the atoms of the molecules of carbon compounds did not take a precise form until the tetravalence of carbon was clearly established. It was, in fact, only after this fundamental principle in the structure of organic molecules had been revealed and it had led to a general point of view and a classification of organic compounds, that it was possible to take up the question of the arrangement in space of the four groups which are combined with the carbon atom and to explain certain phenomena of isomerism by means of considerations on the different arrangement in space of these four groups.

The development of the theoretical conceptions relative to the stereochemical formulas of inorganic compounds followed an entirely analogous course. It was seen first that a large number of elementary metallic atoms have the property of forming complex radicals, MeA_6, in which the metallic atom Me is combined directly with the six groups A, so that these complex radicals must correspond to the structural formula

$$\begin{array}{ccccc} A & & & & A \\ & \diagdown & & \diagup & \\ A & — & Me & — & A \\ & \diagup & & \diagdown & \\ A & & & & A \end{array}$$

The exactitude of this structural formula was established as the result of numerous investigations on the number of ions which the complex inorganic compounds form in aqueous solutions, investigations based especially on the determinations of the electrolytic conductivity of aqueous solutions of these compounds, for the groups directly combined with the central atom remain combined with the latter when the compounds are dissolved in water and consequently take no part in the electrolytic conductivity and do not appear in the form of ions free and independent of the central atom.

A new decisive experimental proof of the structural formula of these complex radicals was furnished by the discovery of a great number of new isomerism phenomena, predicted by the theory, as, for example, coördination polymerism, coördination isomerism, ionization metamerism, hydration isomerism, salt isomerism, isomerism phenomena, of which I had the honor to speak to you, some years ago, in an address made in Haller's laboratory. Thanks to these investigations on the con-

stitution of complex inorganic compounds, the important conception of the coördination index of elements was acquired, a conception which may now be summarized as follows: The coördination index of a large number of elementary atoms is equal to six, i. e., they have the power of combining with six other atoms.

We cannot take up here the nature of the forces which unite the six groups to the central atom; we shall note only that the affinity brought into play may manifest itself either in the form of principal valences or in the form of secondary valences.

As examples of compounds containing a complex radical, MeA_6, we may cite the following:

$$[Co(NO_2)_6]R_3,\ [PtCl_6]R_2,\ [AlF_6]Na_3,\ [Fe(CN)_6]R_4,\ [Co(NH_3)_6]X_3,$$

$$Pt\begin{matrix}(NH_3)_2\\ \\ Cl_4\end{matrix},\ \left[Pt\begin{matrix}NH_3\\ \\ Cl_5\end{matrix}\right]R,\ [Cr(OH_2)_6]X_3,\ \left[\begin{matrix}OH\\ \\ NO\end{matrix}Ru(NH_3)_4\right]X_2, \text{ etc.}$$

The number of compounds containing a radical of this type is very large.

Just as in the discussion of stereochemical problems relating to organic compounds the structural formula, CH_4, of methane serves as basis, so the structural formula, MeA_6, of the complex radicals serves as basis for the study of the configuration in space of inorganic molecules.

The first principal extension of our knowledge of the constitution of the complex radicals MeA_6 was gained experimentally and led to the admission that the six coördination positions of the central elementary atom are equivalent. This conception is derived from the impossibility of preparing isomeric compounds containing complex radicals, $Me\begin{matrix}A_5\\ B\end{matrix}$. We conclude that in the radicals MeA_6, the arrangement of the six groups around the central atom is symmetrical.

Theoretically, three different symmetrical arrangements can be imagined—the plane, the prismatic and the octahedral arrangement.

With the first two of these arrangements we can conceive of three series of isomers of compounds with the complex radicals $Me\begin{matrix}A_4\\ B_2\end{matrix}$; the octahedral arrangement, on the other hand, demands but two. Here again, it was experimental investigation which served to answer the question as to which of the arrangements mentioned corresponds to the configuration of

these complex radicals. By means of numerous researches, it has been possible to show that there are never three series of isomers, but only two, and there are now known for the compounds of cobalt about 30 types of compounds with the complex radicals $\mathrm{Me}\genfrac{}{}{0pt}{}{A_4}{B_2}$ which exist in the form of two series of stereochemical isomers; similar compounds of chromium and platinum are known.

We can conclude with certainty that the six groups occupy the octahedral arrangement around the central atom. The problem of the determination of the configuration formulas of the isomers, i. e., of the determination of the relative positions occupied in the octahedral arrangement by the groups B of the isomeric radicals $\mathrm{Me}\genfrac{}{}{0pt}{}{A_4}{B_2}$, has likewise been solved in a satisfactory manner.

The configuration formulas deduced for the octahedral arrangement for the isomers with the complex radicals $\mathrm{Me}\genfrac{}{}{0pt}{}{A_4}{B_2}$ contain the two groups B in different and opposite positions; in one of the forms they are in a near (*cis*) position and in the other in a distant (*trans*) position.

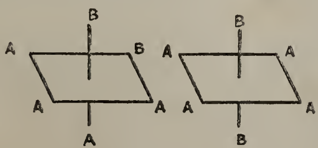


Fig. I

These stereochemical formulas show, therefore, differences analogous to those of the formulas of maleic and fumaric acids, and we could therefore expect differences in properties between the inorganic stereochemical isomers analogous to those found between maleic and fumaric acids. It has been possible to verify experimentally these theoretical previsions. Of the two series of stereochemical isomers, only one shows direct relations with compounds containing in the place of the two groups B a radical forming a closed chain with the central atom, from which we may conclude that only in this series of isomers are the two groups B in a near (*cis*) position, i. e., in a position favorable for the closing of the chain.

With the experimental sanction of these relations and others, it has been possible to determine the configuration formulas of all the isomeric series, and the configurations thus established have been confirmed by the researches on optical isomers, with which their study is related. From the octahedral formula, in fact, we can predict, besides the stereochemical isomers already mentioned, others which belong to the group of isomers with nonsuperposable images, and by the experimental confirmation of these extreme conclusions a new decisive proof for the octahedral formula was obtained, for these phenomena of optical isomerism can neither be foreseen nor explained by any other theoretical conception. Let us first take up briefly the theoretical conclusions deduced from the octahedral arrangement.

The octahedral arrangement leads, for a number of inorganic complex compounds, to configuration formulas with nonsuperposable images. I should like, however, to limit my theoretical conclusions to simple cases easily attacked experimentally. Cases of this kind are found among compounds with the complex radicals $Me\begin{matrix}A_4\\B_2\end{matrix}$, i. e., among the compounds which we have already taken up in our development of stereochemical isomerism. When the composition of the complex radicals $Me\begin{matrix}A_4\\B_2\end{matrix}$ is such that 2 coördinately bivalent groups, such as ethylenediamine or other groups of analogous constitution, are substituted for the four groups A, and the two groups B are in the near (*cis*) position, the space formulas of these compounds are not superposable on their images. We may distinguish three different cases:

a. Compounds with complex radicals $\left[\begin{matrix}A\\B\end{matrix}MeEn_2\right]$. These complex radicals contain two asymmetric tetrahedrons (A, B, En, Me) which, as the result of the different orientation in space of the two molecules of ethylenediamine (En), are not identical.

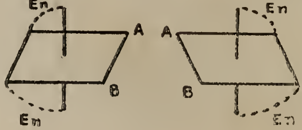


Fig. II

b. Compounds with complex radicals $\left[\begin{matrix} B \\ & MeEn_2 \\ B \end{matrix}\right]$. These complex radicals contain no asymmetric tetrahedral grouping. We therefore have there a kind of molecular asymmetry which we shall designate by the expression "molecular asymmetry I."

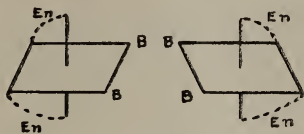


Fig. III

c. Compounds with complex radicals $[MeEn_3]X_3$. These complex radicals contain three equal, coördinately bivalent groups. We shall call this asymmetry "molecular asymmetry II."

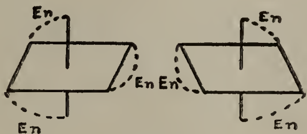


Fig. IV

The stereochemical formulas of the *trans* isomers of all these compounds are superposable on their images and consequently we can expect no optical isomerism for these compounds.

The results of our researches harmonize perfectly with these theoretical deductions. We have been able to resolve into their optically active modifications the *cis* forms of the compounds of all the formula-types indicated above, but all efforts to resolve the *trans* isomers were unsuccessful. We may note, further, that in all cases the two active modifications have equal and opposite rotatory powers.

I shall point out now, in what follows, how these resolutions have been effected in practice and what the properties of the optical isomers are.

Methods of Resolution

Thus far, we have not employed in our researches the spontaneous and biochemical methods of resolution; we have

limited ourselves to the method generally employed in organic chemistry for the resolution of active bases. We caused the halogen salts of the series to be resolved to react with the silver salts of optically active acids, and then separated into their components, by means of fractional crystallization, the mixtures of salts formed. Among the acids which were used, we may mention especially the α-bromocamphorsulphonic acids and Reychler's camphorsulphonic acids.

The α-bromocamphorsulphonic acids are much preferable to the camphorsulphonic acids, for thus far we have been able to resolve only two series of compounds by means of the camphorsulphonates, while we have resolved eight of them with the bromocamphorsulphonates.

Nevertheless, α-bromocamphorsulphonic acid is not a general agent for the resolution, for we have found that different series form partial racemates, so that the resolution is not successful. This, for example, is the case in the 1,2-diamminediethylenediaminecobaltic and the carbonatodiethylenediaminecobaltic series and others.

As regards the resolution by means of the *d*-α-bromocamphorsulphonic and *d*-camphorsulphonic salts, it should be noted that the isolation of the active series forming slightly soluble salts is easy, but the purification of the sometimes exceedingly soluble salts of the series of opposite rotatory power often presents difficulties. To get around these difficulties, we have, in certain cases, retransformed the soluble sulphonates into halogen salts and caused these to react with the *l*-bromocamphorsulphonate or camphorsulphonate of silver, so as to obtain difficultly soluble salts of the series of opposite rotatory power. By this method we have been able to isolate quantitatively the optical isomers.

In certain cases, the *l*-bromocamphorsulphonic acid, which is difficultly accessible, can be replaced by *d*-camphorsulphonic acid, for the solubility of the camphorsulphonates is often the inverse of that of the corresponding α-bromocamphorsulphonates. It is possible, therefore, in preparing the *d*-camphorsulphonate, to first isolate one of the series, then, starting with the salts remaining in the mother liquor, to prepare the *d*-camphorsulphonate of the opposite series. It goes without saying that the order of preparation of the bromocamphorsulphonates and camphorsulphonates can be reversed.

We likewise made numerous attempts to resolve the tartrates of different series by subjecting them to fractional crystallizations, but the results obtained were not satisfactory. On the other hand, we were able to determine that the resolution compounds with trivalent radicals, corresponding

to the general formula $[MeEn_3]X_3$, can be effected with remarkable success by means of mixed salts, such as the chloride tartrates and bromide tartrates,

$$[MeEn_3]\begin{matrix} Cl \\ C_4H_4O_6 \end{matrix} \quad \text{and} \quad [MeEn_3]\begin{matrix} Br \\ C_4H_4O_6 \end{matrix}$$

which do not form partial racemates.

The method of fractional crystallization which we have just described has rendered us great service, but as it involves crystallizations in aqueous solutions it is applicable only to the case of compounds stable in aqueous solution. Therefore compounds with complex radicals containing groups which, by the action of water, are easily dissociated into the form of ions are almost excluded from this method. It is thus that the resolution of the 1,2-chloronitrodiethylenediaminecobaltic salts was effected only with a very great loss of product.

To overcome these difficulties, we devised a method which is applicable to cases where the differences of solubility between the bromocamphorsulphonates or camphorsulphonates of the optical isomers are very large.

This method has, on the one hand, the advantage of not requiring the silver salts of the active acids, which, when the complex radicals contain a halogen, may give rise to secondary reactions, and furthermore avoids a long standing of the salts to be resolved in the aqueous solution, which is quite important in the cases where these salts are easily altered by water. The new method is based on a simple precipitation process. If active ammonium bromocamphorsulphonate is added to a concentrated solution of the racemic compound to be resolved, one of whose active components gives a difficultly soluble bromocamphorsulphonate, the latter is precipitated, in some cases in pure state, in others mixed with a little of the partial racemate. (In the latter case, the precipitated salt is transformed into an easily soluble salt and its solution is again precipitated with ammonium bromocamphorsulphonate.) From the mother liquors from the first precipitation, the series with opposite rotatory power can be isolated by adding the isomeric active ammonium bromocamphorsulphonate. By means of this method, it has been possible to resolve the *cis*-dichlorodiethylenediaminecobaltic series, which, in aqueous solution, is very rapidly transformed into the chloroaquocobaltic series. But the best results have been obtained in the *cis*-chloroisosulphocyanodiethylenediaminecobaltic series, because the *d*-bromocamphorsulphonate of the *l*-rotatory form

and the *l*-bromocamphorsulphonate of the *d*-rotatory form of this series are almost insoluble in water. The importance of the new method has been increased lately by the use of the sodium salt of nitrocamphor, which we shall call sodium camphornitronate. This compound has made possible the resolution of series which could not be resolved by means of the bromocamphorsulphonates and camphorsulphonates. The method of using sodium camphornitronate is the same as that for the ammonium salts of camphor- and bromocamphorsulphonic acids. Likewise, ammonium tartrate has rendered services in one case where the other methods did not succeed. We have found that, for the resolution of irontri-α-dipyridyl, ammonium tartrate can be used in the same way as ammonium camphorsulphonate, ammonium bromocamphorsulphonate and sodium camphornitronate in the other cases.

Summarizing the new points of view bearing on the resolution of inorganic racemic compounds which result from our investigations, we reach the following conclusions:

1. Certain mixed salts, i. e., salts which, besides radicals of active acids, also contain radicals of inactive acids, such as the chloride-tartrates and bromide-tartrates, lend themselves in a peculiar manner to the resolution by fractional crystallization of racemic inorganic compounds.

2. Instead of the method of resolution generally used in organic chemistry, which is based on fractional crystallization and which is often inapplicable to inorganic compounds, advantageous use can be made of a new method, which consists in precipitating one of the active components from the aqueous solution of the racemate by means of the soluble salts of active acids.

General Summary of Active Metallic Compounds

Let us pass now to a general summary of the active metallic compounds thus far obtained. By fractional crystallization, the following series of metallic compounds have been resolved into their active modifications:

1. 1,2-Chloroamminediethylenediaminecobaltic series.
2. 1,2-Bromoamminediethylenediaminecobaltic series.
3. Tetraethylenediamine-μ-aminoperoxodicobaltic series.
4. Tetraethylenediamine-μ-aminonitrodicobaltic series.

The resolution of these four series was effected with the bromocamphorsulphonates. The 1,2-dinitrodiethylenediaminecobaltic series was resolved by means of the bromocamphorsulphonates and the camphorsulphonates. For the tri-

ethylenediaminecobaltic and triethylenediaminerhodic series, the resolution succeeded with the chloride-tartrates; for the triethylenediaminecobaltic series, with the bromide-tartrates also.

By precipitation of concentrated solutions of racemates with ammonium *d*-bromocamphorsulphonate, we have been able to obtain the difficultly soluble bromocamphorsulphonates of the following series:

1. *d*-Chloroamminediethylenediaminecobaltic series.
2. *d*-Bromoamminediethylenediaminecobaltic series.
3. 1,2-*l*-Dichlorodiethylenediaminecobaltic series.
4. *d*-Chloronitrodiethylenediaminecobaltic series.
5. *l*-Chloroisosulphocyanodiethylenediaminecobaltic series.
6. *l*-Dichlorodiethylenediaminechromic series.

With ammonium *d*-camphorsulphonate, we were able to precipitate the *l*-chloronitrodiethylenediaminecobaltic and *l*-bromonitrodiethylenediaminecobaltic camphorsulphonates; finally, with ammonium *d*-tartrate, the tartrate of *l*-rotatory irontri-β-dipyridyl; and with sodium camphornitronate, the *d*-triethylenediaminechromic and *l*-triethylenediaminerhodic camphornitronates.

Let us add to this enumeration the active metallic compounds prepared by chemical reactions from active compounds obtained by resolution. They are the following:

$$\left[\begin{matrix} H_2O & \\ & CoEn_2 \\ H_3N & \end{matrix}\right]X_3,\quad \left[\begin{matrix} H_3N & \\ & CoEn_2 \\ H_3N & \end{matrix}\right]X_3,$$

$$\left[OC\begin{matrix} O. \\ \\ O. \end{matrix}CoEn_2\right]X,\quad \left[\begin{matrix} O_2N & \\ & CoEn_2 \\ SCN & \end{matrix}\right]X,$$

$$\left[\begin{matrix} H_2O & \\ & CoEn_2 \\ O_2N & \end{matrix}\right]X_2,\quad \left[En_2Co\begin{matrix} .NH_2. \\ \\ .OH. \end{matrix}CoEn_2\right]X_4,$$

$$\left[En_2Co\begin{matrix} .NO_2. \\ \\ .NH_2. \end{matrix}CoEn_2\right]X_4$$

By classifying all these series of compounds according to the radical types which characterize them, we obtain the following summary:

a. Compounds with the complex radicals $\left[\begin{matrix} A & \\ & MeEn_2 \\ B & \end{matrix}\right]$ (asymmetric metallic atom):

$$(1)\left[\begin{matrix}Cl & \\ & CoEn_2\\ H_3N & \end{matrix}\right]X_2,\quad (2)\left[\begin{matrix}Br & \\ & CoEn_2\\ H_3N & \end{matrix}\right]X_2,\quad (3)\left[\begin{matrix}Cl & \\ & CoEn_2\\ O_2N & \end{matrix}\right]X,$$

$$(4)\left[\begin{matrix}Cl & \\ & CoEn_2\\ SCN & \end{matrix}\right]X,\quad (5)\left[\begin{matrix}O_2N & \\ & CoEn_2\\ SCN & \end{matrix}\right]X,\quad (6)\left[\begin{matrix}H_2O & \\ & CoEn_2\\ H_3N & \end{matrix}\right]X_2,$$

$$(7)\left[\begin{matrix}H_2O & \\ & CoEn_2\\ O_2N & \end{matrix}\right]X_2,\quad (8)\left[\begin{matrix}H_2O & \\ & CoEn_2\\ SCN & \end{matrix}\right]X_2,$$

$$(9)\left[En_2Co\begin{matrix}.O_2.\\ \\ .NH_2.\end{matrix}CoEn_2\right]X_4,\quad (10)\left[En_2Co\begin{matrix}.OH.\\ \\ .NH_2.\end{matrix}CoEn_2\right]X_4,$$

$$(11)\left[En_2Co\begin{matrix}.NO_2.\\ \\ .NH_2.\end{matrix}CoEn_2\right]X_4$$

b. Compounds with complex radicals $[A_2MeEn_2]$ (molecular asymmetry I):

$$(1)\left[\begin{matrix}O_2N & \\ & CoEn_2\\ O_2N & \end{matrix}\right]X,\quad (2)\left[\begin{matrix}Cl & \\ & CoEn_2\\ Cl & \end{matrix}\right]X,\quad (3)\left[OC\begin{matrix}O\\ \\ O\end{matrix}CoEn_2\right]X,$$

$$(4)\left[\begin{matrix}H_3N & \\ & CoEn_2\\ H_3N & \end{matrix}\right]X_3,\quad (5)\left[\begin{matrix}Cl & \\ & CrEn_2\\ Cl & \end{matrix}\right]X$$

c. Compounds with complex radicals $[MeEn_3]$ (molecular asymmetry II):

(1) $[CoEn_3]X_3$, (2) $[CrEn_3]X_3$, (3) $[RhEn_3]X_3$, (4) $[Dip_3Fe]X_2$

We thus know, in all, the two active forms of 20 series of metallic compounds, and these compounds are derived from 4 different elements: cobalt, chromium, iron and rhodium.

Characteristics of the Active Metallic Compounds

After this general summary of the active compounds thus far obtained, we pass to the characterization of these compounds.

a. Cobalt Compounds

The active compounds derived from cobalt which we have prepared may be classified in the following manner:

1. Diacidotetraminecobaltic series.
2. Acidopentaminecobaltic series.
3. Hexaminecobaltic series.
4. Series of active compounds with two asymmetric cobalt atoms.

5. Series of active compounds with asymmetric carbon and cobalt.

Of the diacidodiethylenediaminecobaltic salts, we may mention the following:

$$(1)\left[\begin{matrix}O_2N & \\ & CoEn_2 \\ O_2N & \end{matrix}\right]X,\quad (2)\left[\begin{matrix}O_2N & \\ & CoEn_2 \\ Cl & \end{matrix}\right]X,\quad (3)\left[\begin{matrix}SCN & \\ & CoEn_2 \\ Cl & \end{matrix}\right]X,$$

$$(4)\left[\begin{matrix}O_2N & \\ & CoEn_2 \\ Br & \end{matrix}\right]X,\quad (5)\left[\begin{matrix}Cl & \\ & CoEn_2 \\ Cl & \end{matrix}\right]X,\quad (6)\left[\begin{matrix}SCN & \\ & CoEn_2 \\ O_2N & \end{matrix}\right]X,$$

$$(7)\left[OC\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle CoEn_2\right]X$$

The stability of these compounds, dissolved in water, is very different. Thus, the dinitrodiethylenediaminecobaltic salts can stand for months in aqueous solution without their rotatory power undergoing any change, while, on the other hand, the nitroisosulphocyanodiethylenediaminecobaltic salts are already less stable, for after four months we observed a decrease of rotatory power amounting to about one-fourth of the initial rotatory power.

The salts of the chloronitro series behave in a still different manner. The optical activity increases rapidly to a maximum value, which is about twice the first value; they show, therefore, the phenomenon of mutarotation. It has been possible to determine the cause of this phenomenon; we have isolated the salts with increased rotation, they belong to the nitroaquodiethylenediaminecobaltic series, $\left[\begin{matrix}O_2N & \\ & CoEn_2 \\ OH_2 & \end{matrix}\right]X_2$. The phenomenon of mutarotation is therefore the result of a hydration. But the nitroaquodiethylenediaminecobaltic series undergoes, in aqueous solution, an ever-increasing racemization, so that the rotatory power, after having attained a maximum, again diminishes, disappearing completely at the end of a certain time (2 days).

The dichloro series, $[Cl_2CoEn_2]X$, behaves in an entirely different manner. The rotatory power, which is at first very large, diminishes rapidly and disappears completely after a few hours. We have here, therefore, a case of complete racemization taking place very rapidly. Likewise, the active salts of the carbonatodiethylenediaminecobaltic series behave in a very interesting manner. They are stable in cold aqueous solution, but if their solutions are heated the activity

diminishes and it disappears completely if the temperature is raised to 90°. We have determined that the product formed is of the racemic carbonate series, and it is formed without its being possible, as in the other series, to observe the formation of intermediate aquocobaltic salts. This phenomenon of racemization completely resembles, therefore, the phenomena of autoracemization observed in organic chemistry. Let us pass, now to an analysis of the chemical reactions of the active diacidocobaltic compounds. In the chloronitro compounds, we can substitute the chlorine by other acid radicals without the production of any marked racemization. Thus, by the action of sodium nitrite are obtained the active dinitro salts and by the action of potassium sulphocyanate the active nitroisosulphocyanates:

$$\left[\begin{array}{l} Cl \\ \quad CoEn_2 \\ O_2N \end{array}\right]X + NaNO_2 = \left[\begin{array}{l} O_2N \\ \quad CoEn_2 \\ O_2N \end{array}\right]X + NaCl$$

$$\left[\begin{array}{l} Cl \\ \quad CoEn_2 \\ O_2N \end{array}\right]X + KCNS = \left[\begin{array}{l} SCN \\ \quad CoEn_2 \\ O_2N \end{array}\right]X + KCl$$

For the chloroisosulphocyanates, the reactions do not take place so sharply. Thus with sodium nitrite is obtained, besides the active nitroisosulphocyanate series, the racemic series also. The same thing occurs with the active dichloro salts which, with potassium carbonate, give much of the racemic carbonate together with a small quantity of the active salt. A complete racemization takes place when hydrochloric acid in alcoholic solution is made to react on a salt of the active carbonate series; completely inactive 1,2-dichloro salt is formed. In the same way the action of dilute mineral acids on the active carbonate salts produces only inactive diaquodiethylenediaminecobaltic salts. All these facts show that, in certain reactions, intramolecular replacements in the asymmetric radicals take place very easily.

The active acidopentamine compounds which we have thus far prepared correspond to the formulas

$$\left[\begin{array}{l} Cl \\ \quad CoEn_2 \\ H_3N \end{array}\right]X_2 \text{ and } \left[\begin{array}{l} Br \\ \quad CoEn_2 \\ H_3N \end{array}\right]X_2$$

These compounds are stable in cold or slightly warm aqueous solution; however, when they remain a long time in solution, they are partially transformed into aquoamminediethylenediaminecobaltic salts, but without undergoing racemization. By the action of silver nitrate it is possible to transform the

bromo series into the aquoamminecobaltic series which we were able to isolate in the pure state. (Its salts show in 0.5 per cent. solution a mean rotatory power $[\alpha]_D = 64°$ and $[M]_D = 392°$.)

If, on the other hand, the aquoamminecobaltic series is prepared by the action of an alkali on the bromo salts in concentrated solution, total racemization occurs. There seems to be here an important starting point for the experimental study of the problem of Walden's optical inversion.

The way in which the bromo series behaves when it reacts with liquid ammonia is very interesting. There are formed the two stereochemical isomers of the diamminediethylenediamine-cobaltic series, and while the *cis* form shows a rotatory power, the *trans* form is, as demanded by the theory, entirely optically inactive.

The group of active cobalt compounds with trivalent complex radicals obtained thus far consists of the following series:

$$[CoEn_3]X_3,\ \left[Co{\begin{matrix}(NH_3)_2\\ \\ En_2\end{matrix}}\right]X_3,\ \left[{\begin{matrix}HOH_2N & \\ & CoEn_2\\ H_3N & \end{matrix}}\right]X_3,\ \left[Co{\begin{matrix}Tn\\ \\ En_2\end{matrix}}\right]X_3,$$

$$\left[Co{\begin{matrix}Pn\\ \\ En_2\end{matrix}}\right]X_3,\ \left[{\begin{matrix}H_2O & \\ & CoEn_2\\ H_3N & \end{matrix}}\right]X_3$$

The triethylenediaminecobaltic series shows the strongest rotation (bromide, $[\alpha]_D = 117°$, $[M]_D = 600°$), and the amminehydroxylaminediethylenediaminecobaltic series has a rotatory power almost as large (bromide in 0.25 per cent. solution, $[\alpha]_D = 112°$, $[M]_D = 545°$). The diamminediethylenediaminecobaltic series shows the smallest rotatory power (bromide, $[\alpha]_D = 38°$, $[M]_D = 172°$).

Let us consider now the cobalt compounds with complex radicals containing two asymmetric cobalt atoms.

By causing ethylenediamine to react on the octammine-μ-aminodicobaltic salts are obtained tetraethylenediamine-μ-aminoperoxodicobaltic salts. The general formula for these salts is the following:

$$\left[En_2Co{\begin{matrix}{}^{III}.NH_2.{}^{IV}\\ \\ .O_2\ .\end{matrix}}CoEn_2\right]X_4$$

containing two asymmetric cobalt atoms. It has been possible to resolve this series by means of the bromocamphorsulphonates into two active forms with opposite rotatory powers.

These active forms have a rotatory power of exceptional magnitude; the bromides, for example, show a specific rotatory

power of 824°, whence is obtained a molecular rotatory power of 6725°.

Still more interesting results have been obtained with the tetraethylenediamine-μ-aminonitrodicobaltic salts, which were prepared by the action of nitrous acid on the tetraethylenediamine-μ-aminoperoxodicobaltic series. They have a strong red-orange color. We have obtained three different *d*-bromocamphorsulphonates:

1. A difficultly soluble *d*-bromocamphorsulphonate derived from the *d*-μ-aminonitro series.

2. A much more easily soluble *d*-bromocamphorsulphonate derived from the *d*-aminonitro series. The salts prepared from these two bromocamphorsulphonates have equal but opposite rotatory powers.

3. A *d*-bromocamphorsulphonate of intermediate solubility, which gives inactive μ-aminonitro salts not resolvable into active forms.

By combining the active *d*- and *l*-salts, there are obtained racemic salts which are different from the inactive salts derived from the bromocamphorsulphonate of intermediate solubility.

We therefore have here a case analogous to that of the tartaric acids. We have, on the one hand, two active forms with opposite rotatory powers which, in equimolecular mixture, give a racemic form corresponding to "racemic acid." On the other hand, we have a series which is inactive by intramolecular compensation and corresponds to mesotartaric acid or "nonresolvable tartaric acid."

We may conclude from these facts that the constitutional formula of the tetraethylenediamine-μ-aminonitro series is symmetrical, i. e., that the nitro group is combined in the same way to the two cobalt atoms.

Let us note, likewise, that it is possible to transform the active salts into nonresolvable salts, a fact analogous to that observed for the tartaric acids by Jungfleisch, who, by heating tartaric acid at 200°, obtained mesotartaric acid. In the case we are considering, the transformation takes place under analogous conditions, for by vigorously boiling a solution of one of the active salts, a part of the active salt is transformed into a nonresolvable salt.

Let us conclude our summary of the results obtained with the active cobalt salts by adding that we have likewise prepared compounds containing at the same time a complex asymmetric radical and an asymmetric carbon, by the action of active propylenediamine on the dichlorodiethylenediamine-

cobaltic salts. As the propylenediamine enters the complex radical in the *cis* position, the two molecules of ethylenediamine which belong to the complex are perforce in the positions which condition the asymmetric arrangement of the complex radical. But as this arrangement leads to two stereochemical configurations, we should expect the formation of two isomeric active series, *D-l* and *L-d*, the salts of which should be distinguished by their optical activities.

These theoretical previsions have been confirmed experimentally. We obtained two series, which are distinguished especially by the different solubilities of their salts and their optical activity.

b. Chromium Compounds

Thus far we have been able to prepare the optical isomers of two series of chromium compounds. They are the dichlorodiethylenediaminechromic salts, which show the molecular asymmetry I, and the triethylenediaminechromic salts, which exhibit the molecular asymmetry II. The dichlorodiethylenediaminechromic salts are very slightly stable in aqueous solution, like their analogues in the cobaltic series. Their molecular rotatory power, which is about 500°–600°, decreases very rapidly, and after a few hours the solutions have become entirely inactive. It is probable that this phenomenon of racemization is the result of the intermediate formation of hydrated salts; however, we still lack a thorough experimental study of this subject.

The triethylenediaminechromic salts are, on the contrary, much more stable. Their molecular activity in cold aqueous solution is about 340° and hardly undergoes any change on long standing of the salts in solution. It is only when the solutions are evaporated that the optical activity diminishes.

c. Iron Compounds

All the active compounds of cobalt and chromium thus far obtained contain ethylenediamine as a constituent group of the complex molecule. It was therefore important to effect the resolution of compounds containing in the place of ethylenediamine other cöordinately bivalent groups and to prove thus that the ethylenediamine is not absolutely necessary for the formation of active metallic compounds. Moreover, in order to be able to study the influence of the central atom on the rotatory power of complex inorganic compounds, it was desirable to prepare optically active compounds derived from other metallic elements.

These considerations led us to attempt the resolution of

the tri-α-dipyridylferrous compounds, $[FeDpy_3]X_2$. The discovery of these iron compounds is due to F. Blau, and they present a more general interest because they possess an intense red color and contain the iron in a masked form, recalling the properties of hemoglobin. After numerous unsuccessful attempts, we have been able to prepare the tartrate of the *l*-rotatory series of irontri-α-dipyridyl by saturating the aqueous solution of the racemic bromide with ammonium *d*-tartrate. It was possible to transform the tartrate thus obtained into different salts, such as the iodide, the bromide, etc., and these salts were found to possess a very large rotatory power. The specific rotatory power varies around 500°, which, for the bromide, corresponds to a molecular rotatory power of 4000°.

In the solid state, these iron salts remain active indefinitely, but in aqueous solution they racemize very rapidly. After one-half hour, the rotatory power has already decreased by one-half, and after a few hours the solutions of these salts have become entirely inactive. This phenomenon of racemization is certainly caused by a partial decomposition of the active salts, with separation of a small quantity of α-dipyridyl, which, in aqueous solution, forms a dynamic equilibrium with the nondecomposed tri-α-dipyridylferrous salt. Our further studies must be applied to the investigation of active iron compounds showing greater stability.

The results obtained thus far with iron compounds show that the iron atom can likewise function as the center of asymmetric molecules showing optical activity. Moreover, they show that the activity of the optical isomers thus far described is not related with the specific nature of ethylenediamine but that the phenomenon also manifests itself when the ethylenediamine is replaced by other groups. Finally, let us emphasize the fact that in the iron compounds we have to do with derivatives of a bivalent metallic atom, while the active compounds of the other elements are derived from tri- and tetravalent metallic atoms.

d. Rhodium Compounds

Although we do not, up to the present, know any rhodium compounds containing groups with two coördinative valences, we have been able to prepare the triethylenediaminerhodic salts. If sodium chlororhodiate, $[RhCl_6]Na_3$, is introduced into monohydrated ethylenediamine, it dissolves rapidly with evolution of heat and formation of a slightly yellow solution. This solution contains triethylenendiaminerhodic chloride, $[RhEn_3]Cl_3$, which can be isolated in beautiful, colorless crys-

tals. It has been possible to obtain the active triethylenediaminerhodic salts by two different methods.

The first consists in precipitating the concentrated solution of the chloride with sodium camphornitronate. The camphornitronate which separates belongs to the levo series and by adding potassium iodide to the mother liquor the iodide of the dextro series is obtained.

The resolution is still better effected by the method used for the resolution of the triethylenediaminecobaltic salts. Triethylenediaminerhodic chloride is made to react with a molecule of silver tartrate and the solution is concentrated until crystals are formed. The chloride-tartrate of the levo series separates in the form of colorless crystals, very clear and beautifully developed; the concentrated mother liquor gives a white salt of chalky appearance, which is the chloride-tartrate of the dextro series.

The chloride-tartrates can easily be transformed into other salts. The specific rotatory power of these salts varies between 70° and 80°, which corresponds to a molecular rotatory power of about 300°.

Relations between the Optical Activity, the Configuration and the Constitution of the Complex Inorganic Compounds

The greater number of the active metallic compounds which we have studied contain a complex radical [$MeEn_2$], whose formula in space is not superposable on its image and can thus present itself under two stereochemical forms.

We might inquire if all the compounds presenting the same configuration of the radical [$MeEn_2$] deviate the plane of polarized light in the same direction. We were easily able to establish that this is not the case, but that the direction of the rotatory power depends on the nature of the radicals which occupy the two other coördination positions of the central atom and on the nature of that central atom.

This is derived from the fact that we have been able to prepare compounds of opposite rotatory powers by chemical reactions which are certainly not accompanied by a change in configuration. Let us give some examples: Starting from the *l*-dichlorodiethylenediaminecobaltic series, we have obtained, by making it react with potassium carbonate, the *d*-carbonatodiethylenediaminecobaltic series:

$$\underset{\text{Levo}}{\left[\begin{matrix}Cl & \\ & CoEn_2 \\ Cl & \end{matrix}\right]Cl} + K_2CO_3 \longrightarrow 2KCl + \underset{\text{Dextro}}{\left[OC\begin{matrix}\diagup O \diagdown \\ \diagdown O \diagup\end{matrix}CoEn_2\right]Cl}$$

Likewise, the *l*-chloroisosulphocyanodiethylenediaminecobaltic salts are transformed, by the action of sodium nitrite, into *d*-nitroisosulphocyanodiethylenediaminecobaltic salts:

$$\underset{\text{Levo}}{\left[\begin{matrix}Cl & \\ & CoEn_2 \\ SCN & \end{matrix}\right]X} + NaNO_2 \longrightarrow NaCl + \underset{\text{Dextro}}{\left[\begin{matrix}O_2N & \\ & CoEn_2 \\ SCN & \end{matrix}\right]X}$$

Moreover, by reduction of the salts of the *l*-tetraethylenediamine-μ-aminoperoxodicobaltic series are obtained the salts of the *d*-tetraethylenediamine-μ-amino-oldicobaltic series:

$$\underset{\text{Levo}}{\left[En_2Co \begin{matrix}.O_2\ .\\ \\ .NH_2.\end{matrix} CoEn_2\right]X_4} \longrightarrow \underset{\text{Dextro}}{\left[En_2Co \begin{matrix}.OH\ .\\ \\ .NH_2.\end{matrix} CoEn_2\right]X_4}$$

Finally, by the action of nitrous acid on the tetraethylenediamine-μ-aminoperoxodicobaltic salts is obtained, starting from the *l*-series, the *d*-series of tetraethylenediamine-μ-aminonitrodicobaltic salts:

$$\underset{\text{Levo}}{\left[En_2Co \begin{matrix}.O_2\ .\\ \\ .NH_2.\end{matrix} CoEn_2\right]X_4} \longrightarrow \underset{\text{Dextro}}{\left[En_2Co \begin{matrix}.NO_2.\\ \\ .NH_2.\end{matrix} CoEn_2\right]X_4}$$

On the other hand, we have been able to establish the following interesting law: the active isomeric series which give, with the same active acids, the less soluble salts show the same stereochemical configuration of the radical $[MeEn_2]$. This law is demonstrated by the following facts:

The *d*-chloronitro series and the *l*-chloroisosulphocyano series give with *d*-bromocamphorsulphonic acid salts which are much less soluble than those formed with the *l*-acid. It is proved that they correspond to the same stereochemical configuration by the fact that, by the action of potassium sulphocyanide on a salt of the *d*-chloronitro series and of sodium nitrite on a salt of the *l*-isosulphocyano series, the same *d*-rotatory nitroisosulphocyano series is obtained:

$$\left[\begin{matrix}Cl & \\ & CoEn_2 \\ O_2N & \end{matrix}\right]X + KSCN = KCl + \left[\begin{matrix}SCN & \\ & CoEn_2 \\ O_2N & \end{matrix}\right]X$$

$$\left[\begin{matrix}Cl & \\ & CoEn_2 \\ SCN & \end{matrix}\right]X + KNO_2 = KCl + \left[\begin{matrix}O_2N & \\ & CoEn_2 \\ SCN & \end{matrix}\right]X$$

These transformations may be represented by the following scheme:

$$\text{Give difficultly soluble } d\text{-bromocamphorsulphonates}\left\{\begin{array}{c} \left[\begin{array}{ll} \mathrm{Cl} & \\ & \mathrm{CoEn_2} \\ \mathrm{O_2N} & \end{array}\right]\mathrm{X} \\ \text{Dextro} \\ \left[\begin{array}{ll} \mathrm{Cl} & \\ & \mathrm{CoEn_2} \\ \mathrm{SCN} & \end{array}\right]\mathrm{X} \\ \text{Levo} \end{array}\right. \begin{array}{c} \searrow \\ \\ \nearrow \end{array} \begin{array}{c} \left[\begin{array}{ll} \mathrm{O_2N} & \\ & \mathrm{CoEn_2} \\ \mathrm{SCN} & \end{array}\right]\mathrm{X} \\ \text{Dextro} \end{array}$$

Another fact of the same nature is the following: the *l*-tetraethylenediamine-μ-aminoperoxodicobaltic series furnishes a difficultly soluble *d*-bromocamphorsulphonate, while the *d*-tetraethylenediamine-μ-aminonitrodicobaltic series gives a difficultly soluble *d*-bromocamphorsulphonate.

Now, the *l*-tetraethylenediamine-μ-aminoperoxodicobaltic series is transformed by the action of nitrous acid into the *d*-tetraethylenediamine-μ-aminonitrodicobaltic series, proving that the configuration of the $[\mathrm{CoEn_2}]$ groups of these series is identical.

We may summarize the phenomena observed in the following manner: The compounds of the series with identical asymmetry show parallel processes of solubility in their salts with active acids, but the direction of the rotatory power of the salts in question is not necessarily the same.

It is on the basis of these new ideas that we can study in more detail the relations between the rotatory power and the composition of the asymmetric molecules.

Classifying the series with identical configuration in the order of the magnitude and direction of their molecular rotatory powers, we obtain the following summary:

$$\begin{array}{cccc} \left[\mathrm{En_2Co}\begin{array}{c} .\mathrm{OH}\,. \\ \\ .\mathrm{NH_2}. \end{array}\mathrm{CoEn_2}\right]\mathrm{X_4}, & [\mathrm{Cl_2CoEn_2}]\mathrm{X}, & [\mathrm{Cl_2CrEn_2}]\mathrm{X}, & [\mathrm{RhEn_3}]\mathrm{X}, \\ -6723^\circ & -550^\circ & -400^\circ & -350^\circ \end{array}$$

$$\begin{array}{ccc} \left[\begin{array}{ll} \mathrm{Cl} & \\ & \mathrm{CoEn_2} \\ \mathrm{SCN} & \end{array}\right]\mathrm{X_2}, & \left[\begin{array}{ll} \mathrm{Cl} & \\ & \mathrm{CoEn_2} \\ \mathrm{O_2N} & \end{array}\right]\mathrm{X_3}, & \left[\begin{array}{ll} \mathrm{H_3N} & \\ & \mathrm{CoEn_2} \\ \mathrm{H_2O} & \end{array}\right]\mathrm{X_3}, \\ -200^\circ & +74^\circ & +124^\circ \\ \left[\begin{array}{ll} \mathrm{O_2N} & \\ & \mathrm{CoEn_2} \\ \mathrm{O_2N} & \end{array}\right]\mathrm{X}, & \left[\begin{array}{ll} \mathrm{O_2N} & \\ & \mathrm{CoEn_2} \\ \mathrm{H_2O} & \end{array}\right]\mathrm{X_2}, & \left[\begin{array}{ll} \mathrm{H_3N} & \\ & \mathrm{CoEn_2} \\ \mathrm{H_3N} & \end{array}\right]\mathrm{X_3}, \\ +145^\circ & +165^\circ & +172^\circ \\ \left[\begin{array}{ll} \mathrm{H_3N} & \\ & \mathrm{CoEn_2} \\ \mathrm{Cl} & \end{array}\right]\mathrm{X_2}, & \left[\begin{array}{ll} \mathrm{H_3N} & \\ & \mathrm{CoEn_2} \\ \mathrm{Br} & \end{array}\right]\mathrm{X_2}, & \left[\begin{array}{ll} \mathrm{O_2N} & \\ & \mathrm{CoEn_2} \\ \mathrm{SCN} & \end{array}\right]\mathrm{X}, \\ +172^\circ & +180^\circ & +200^\circ \end{array}$$

$$\left[OC{\overset{O}{\underset{O}{\lessgtr}}}CoEn_2\right]X, \quad [CrEn_3]X_3, \quad [CoEn_3]X_3,$$
$$+280^\circ \qquad\qquad +340^\circ\text{–}370^\circ \qquad +600^\circ$$

$$\left[En_2Co\begin{matrix}.OH.\\ \\ .NH_2.\end{matrix}CoEn_2\right]X_4, \quad \left[En_2Co\begin{matrix}.NO_2.\\ \\ .NH_2.\end{matrix}CoEn_2\right]X_4$$
$$+990^\circ \qquad\qquad +1300^\circ\text{–}1400^\circ$$

As a result, the rotatory power is seen to vary between very wide limits and all the groups forming part of the asymmetric complex radical have an influence on the value of the rotatory power. It is seen, likewise, that the nature of the central atom has a capital influence on the magnitude and the direction of the rotatory power, for the rotatory powers of the triethylenediaminecobaltic, -chromic and -rhodic salts, as well as those of the dichlorodiethylenediaminecobaltic and -chromic salts, are entirely different. The compounds of chromium have a smaller rotatory power than the cobalt compounds, but this difference is not equal in the different series; it is about 150° for the dichloro salts, while it is about 250° for the salts containing the triethylenediamine complex radical. The magnitude of the rotatory powder depends, therefore, on a special factor, the value of which is determined by the particular relations which exist between the central atom and the groups which it unites in the complex radicals.

Let us add that the triethylenediaminerhodic salts deviate the plane of polarized light almost as much to the left as the triethylenediaminechromic salts of the same configuration deviate it to the right.

The values for the rotatory powers which served for our theoretical deductions were determined under experimental conditions as nearly comparable as possible; nevertheless, these values probably do not yet give an exact measure of the relative magnitudes of these rotatory powers, and this for the following reasons: The magnitude of the rotatory power often depends to a very high degree on the concentration of the solutions of the salts, and, as near as we can judge thus far, the activity is greater the more dilute the solution. This is probably due to the compounds in the undissociated state having a smaller rotatory power than their asymmetric cations, and it will be necessary, therefore, in order to obtain comparable values, to determine the rotatory power of the undissociated compounds and of their cations. Moreover, it is to be noted that almost all the compounds studied thus far are colored and show very large rotatory dispersions, so that it will be neces-

sary to make exact studies on the relations which exist between the magnitude of the rotatory power and the wave length of the light.

I hope that the researches which we have begun in this direction will lead to precise ideas on the influence of the different atomic groups of the complex radicals on the optical activity.

To end our review, let us consider briefly the consequences of the results thus far obtained for the theory of valence and for stereochemistry.

Our experiments show in the first place that it is of secondary importance for the stability of the molecules of the complex compounds whether the atoms are united by principal valences or by secondary valences. For the study of the structure of inorganic compounds, secondary valences assume an equal importance with principal valences. This naturally leads us to admit that there is no essential difference between the affinities brought into play by the principal valences and the secondary valences. We probably have to do with affinity forces which are distinguished only in magnitude and not in quality and the difference between which does not manifest itself in any notable manner except when the atomic unions which they produce are so different that the ones lead to compounds of great stability and the others to compounds which are slightly stable.

The question of knowing what secondary causes (migrations of electrons, etc.) may lead to a more pronounced differentiation between the atomic unions produced by principal and secondary valences is independent of the question of the nature of the affinity forces which determine the structure of complex inorganic molecules.

As to what concerns stereochemistry, our studies have led us to the probable conclusion that all elementary atoms, in so far as they can function as the central atom of stable complex radicals, are capable of forming compounds showing optical isomerism. Moreover, it has been shown that the optical isomerism is not necessarily due to the different nature of the groups combined with the central atom, but that every asymmetric configuration leads to optical isomerism, even if the constituent parts of the molecular grouping are equal.

We come back then, to the principle which Pasteur first formulated and which admits that every molecule having no plane of asymmetry, i. e., showing structural asymmetry, must always exist in the form of two oppositely active optical modifications. The isomerism phenomena related with the molec-

ular asymmetry of metallic compounds, with asymmetric cobalt, with asymmetric carbon, with asymmetric nitrogen, with the molecular asymmetry of the inositols, etc., are therefore only special cases resulting from this general principle, a principle from which the possibility of numerous other cases of optical isomerism can still be predicted.

The end of future investigations, then, will be to determine what other new cases of optical isomerism, foreseen through our conceptions on the arrangement in space of inorganic molecules, can be realized experimentally.

OBITUARY

L. P. CAILLETET[1]

L. P. Cailletet, known to all chemists and physicists by his work on the liquefaction of gases, died on January 5th, after a short illness. He was born at Châtillon-sur-Seine, September 21, 1832, and thus lived to be over 80 years of age. From his earliest youth he was familiar with the processes involved in blast furnaces and the working of iron. He studied in Paris at the Ecole Superiéure des Mines and his first scientific work was in connection with the cementation and puddling processes. He showed that iron is permeable to gases at high and low temperatures. He next undertook the study of the properties of gases under high pressures. In the course of this work he developed the method for the liquefaction of gases based on the principle of the sudden expansion of the compressed gas. His results with carbon dioxide, carbon monoxide and oxygen were embodied in a sealed communication which was opened December 27, 1877, on receipt of the news that Pictet, of Geneva, had likewise effected the liquefaction of oxygen. About this time, Mathias became associated with Cailletet as his assistant and within the next few years these two men carried out their famous work on the liquefaction of the so-called permanent gases.

In 1893 Cailletet began a series of studies on the resistance offered by the air to moving bodies. By means of balloons carrying ingeniously devised forms of apparatus, he was able to obtain samples of air from different heights and to get accurate thermometric and barometric data and even photographs. He founded what eventually became an International Commission of Scientific Aeronautics for the purpose of making systematic meteorological observations with test balloons. His activities in these lines brought him into prominence in

[1] This note is based on a sketch by Raoult Pictet in the Chem. Ztg., **37**, 177.

the Aero Club of France, and he exerted a most beneficial influence in its affairs.

REVIEWS

CHURCH'S LABORATORY GUIDE, a Manual of Practical Chemistry for Colleges and Schools, Especially Arranged for Agricultural Students. Revised and Largely Rewritten by EDWARD KINCH, F.I.C., etc., Professor of Chemistry in the Royal Agricultural College, Cirencester. Ninth Edition. New York: D. Van Nostrand Co. 1912. xvi + 368 pp. Price, $2.50.

This book is divided into three parts: Part I, 68 pages, contains introductory laboratory experiments, such as specific gravity, preparation of oxygen and hydrogen, ashes of plants, etc.; Part II, 70 pages, deals with qualitative analysis; Part III, 216 pages, takes up quantitative analysis, and gives methods for fertilizers, feeds, soils, etc. The methods of analysis for fertilizers and feeds are those prescribed by the English Board of Agriculture and Fisheries. They are quite different in some respects from the methods of the Official Agricultural Chemists of North America. The book is intended to include a complete course of laboratory practice for agricultural students. The fact that it has gone into nine editions shows that it has been useful. G. S. F.

ELEMENTARY CHEMICAL THEORY AND CALCULATIONS. By JOSEPH KNOX, D.Sc., Lecturer on Inorganic Chemistry, University of Aberdeen. London: Guerney and Jackson. 1912. pp. vii + 102. Price, 2s.

The author has made a collection of well selected chemical problems and has given a clear explanation of the laws and principles upon which their solution is based. J. E. G.

GRUNDZÜGE DER PHARMAZEUTISCHEN CHEMIE. Von HEINRICH BECKURTS, Geheimer Medizinalrat, o. Professor der pharmazeutischen Chemie und Vorstand des Pharmazeutischen Institutes der Herzogl. Technischen Hochschule zu Braunschweig. Mit 15 Abbildungen im Text und 1 Spektraltafel. I. Band. Anorganische Teil. Leipzig: Verlag von S. Hirzel. 1912. S. xix + 386. Preis, geh., M. 10; geb., M. 11.

As is indicated by the title, this book is intended especially for the student of pharmacy and places special emphasis on the qualitative and quantitative tests as to purity and adulterations, as well as the determination of factors such as melting point, boiling point and specific gravity, according to the requirements of the Pharmacopoeia. J. E. G.

INTRODUCTION TO THE RARER ELEMENTS. By PHILIP E. BROWNING, PH.D., Assistant Professor of Chemistry, Kent Chemical Laboratory, Yale University. Third edition, thoroughly revised. New York: John Wiley & Sons. London: Chapman & Hall, Ltd. 1912. pp. xii + 232. Price, $1.50.

Dr. Browning's book needs little description, so far as the

general characteristics are concerned, to those who have made even a cursory study of the rarer elements. Since the first edition was printed in 1903, it has been before every student of chemistry and has invariably made friends.

The third edition is welcome and contains valuable additions. The new tables and charts of both spark and absorption spectra will prove invaluable to the student wishing to make spectroscopic comparisons. The enlargement of the methods of qualitative separation and of the technical applications of the rarer metals, the inclusion of James' latest chart for the fractionation of the rare earths, and the numerous minor changes and enlargements caused by the advance in chemical knowledge since the last edition appeared, all give additional value to the book.

There is little for the reviewer to criticize for the book is already much more than its title would imply and the work is well done. It may not be amiss, however, to hope that in the next edition Professor Browning may carry much farther the work which he is so capable of doing. Scandium, for example, might well be separated from the rare earths, to which it scarcely belongs, and given a chapter by itself, as is already done with the much rarer element germanium; and the recent work of Sir William Crookes would alone furnish much of the material needed for such a presentation. Considering the growing commercial importance of tungsten and vanadium, the subject matter regarding these two elements could be materially expanded; and this is true of most of the other elements considered. In short, we need in the English language a book whose correct title should be "The Rarer Elements" with "Introduction to" left off.

Let us hope that the next edition will cover completely this subject which Professor Browning can handle so well.

CHARLES L. PARSONS

A SECOND YEAR COURSE OF ORGANIC CHEMISTRY FOR TECHNICAL INSTITUTES. The Carbocyclic Compounds. By F. B. THOLE, B.Sc. (Lond.), Lecturer in Organic Chemistry at the East Ham Technical College. London: Methuen & Co., Ltd. 1912. pp. vii + 186. Price, 2 s. 6 d.

This compact and business-like little volume is one of a series of text-books on Organic Chemistry and is chiefly devoted to the compounds of the aromatic series, though it also contains chapters devoted to the polymethylenes, the Grignard reaction, a list of glucosides, and a brief treatise upon Organic Qualitative Analysis.

The work has obviously been prepared chiefly for use in the author's own classes so that it would not be appropriate

to comment critically upon the selection and arrangement of the topics presented. The reviewer, however, believes that its general usefulness will be somewhat restricted on this account.

The book gives concise and definite information concerning the important organic compounds and those theories which it attempts to treat, but the author has allowed himself to yield to the student's craving for unqualified generalizations to an extent which sometimes goes beyond the limits of accuracy. It is only fair to add that the facts which should have qualified some of these statements are usually to be found in other portions of the book.

In spite of this defect, the work seems to be a useful and essentially accurate treatise, and the author is especially to be commended for the amount of space which he gives to the subject of Organic Qualitative Analysis. No method of approaching the subject is so well adapted as this to arouse the student's interest, and none teaches so much chemistry in so short a time.

F. J. Moore

Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen insbesondere des Stassfurter Salzlagers. Von J. H. van't Hoff. Herausgegeben von Professor Dr. H. Precht, Neustassfurt, und Professor Dr. Ernst Cohen, Utrecht. Mit einer Gedächtnisrede auf van't Hoff von Professor Dr. Emil Fischer, Exz. Mit 8 Tafeln und 39 Textabbildungen. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. pp. xx + 374. Price, M. 16.

Van't Hoff published, during the years 1897–1908, a series of fifty-two papers dealing with investigations of conditions of formation of oceanic salt deposits. In the conduct of these researches he was assisted by twenty-nine collaborators (of whom it may be noted that English is the native language of at least twelve), and received financial aid from the Königliche Preussische Akademie der Wissenschaften, in whose *Sitzungsberichte* the original papers appeared. These transactions are not generally accessible, and the individual papers are all out of print. A short account of the work was given in two pamphlets published by van't Hoff, one in 1905 and one in 1909, under the title "Zur Bildung der ozeanischen Salzablagerungen," but this extract is not full enough for any one desirous of studying the methods and results in detail. These considerations have led to the publication of the present volume, which contains all of the original papers in full, together with a prefatory note by the editors and an introductory memoir of van't Hoff written by Emil Fischer.

It is unnecessary to give here the titles of the separate papers, since their general tenor is well known; it suffices to

say that they deal with the chlorides and sulphates, and to a lesser extent the borates, of potassium, sodium, magnesium and calcium, their relations to water and to one another. The experimental work was carried out mainly at 25°, but also to some extent at higher temperatures up to 83°; it consists almost entirely of determinations of solubility, of vapor pressure by means of the tensimeter, and of transition points directly by means of the dilatometer. This series of investigations is an object lesson in showing us what may be accomplished with simple experimental means by the thoroughgoing application of certain chemical principles and is an admirable example of the way to attack similar complex problems, to correlate and interpret the observations, and thus to reach conclusions of great significance—all of which would not have been attained except with the aid of these theoretical principles.

In the introduction to the first paper van't Hoff, in 1897, wrote: "When a thorough series of physico-chemical investigations has led to some knowledge of the equilibrium relations which hold when salts enter into, or separate from, aqueous solutions, and determine the formation of hydrates and double salts and the nature of products obtained by double decomposition, then something can be contributed from the physico-chemical side towards the solution of the geologic problem of the formation of the complex natural salt beds." This modest aspiration has been more than fulfilled. Indeed the success attained by van't Hoff in clearing up this problem is such that we are only now beginning to realize its consequences—technical, economic and scientific; of which not the least is that it has stimulated the investigation of complex systems and encouraged people to attack problems which, until recently, were considered insoluble. In conclusion, it may be noted that the experimental work recorded in this volume is now being repeated and amplified under the direction of the "Verband zur wissenschaftlichen Erforschung der deutschen Kalisalzlagerstätten," the formation and plans of which are discussed in the fifty-second and last paper in the volume.

John Johnston

The Freezing-Point, Boiling-Point and Conductivity Methods. By Harry C. Jones, Professor of Physical Chemistry in the Johns Hopkins University. Second edition, completely revised. Easton, Pa.: Chemical Publishing Co. 1912. pp. vii + 75. Price, $1.00.

The appearance of a second, completely revised edition of this booklet will be welcomed in all physico-chemical laboratories. When it first appeared it was the pioneer laboratory

manual of physical chemistry in the English language and as such was cordially received. Notwithstanding the fact that numerous laboratory manuals are now on the market, this little volume still fills an important place. In the new edition several minor corrections have been made, more comprehensive tables of cryoscopic and ebullioscopic constants have been included and an account is given of the author's extension of the boiling-point method to the measurement of ionization in nonaqueous solvents. The chapter devoted to the measurement of electrical conductivity has been subjected to a thorough revision, the method used in the author's laboratory being described in detail. The book appears in a durable and attractive binding. FREDERICK H. GETMAN

TRATTATO DI CHIMICO-FISICA. HARRY C. JONES, Professore di Chimico-fisica nella Università di Baltimora. Traduzione italiana con Note del DOTT. MICHELE GIUA, Assistente nel Laboratorio Chimico della Società d'Incorraggiamento in Milano, con Prefazione del PROF. ETTORE MOLINARI e 81 Incisioni nel Testo. Milano: Ulrico Hoepli. 1913. pp. xx + 611.

The appearance of this Italian translation, shortly after the publication of the Russian edition, is evidence of the popularity of Prof. Jones' well-known book not only at home but abroad as well. In his translation, Dr. Giua has closely followed the fourth English edition, merely adding a few notes here and there on some of the latest developments of the science. The translation seems to have been well done and the mechanical make-up of the book is up to the high standard of the Hoepli publications. C. A. R.

DAS ERDÖL UND SEINE VERWANDTEN. Geschichte, physikalische und chemische Beschaffenheit, Vorkommen, Ursprung, Auffindung und Gewinnung des Erdöls. Von DR. h. c. HANS VON HÖFER, k. k. Hofrat, em. o. ö. Professor an der k. k. Montanistischen Hochschule in Leoben. Dritte, vermehrte Auflage. Mit 33 Abbildungen im Text und einer Tafel. Neues Handbuch der Chemischen Technologie (Bolley's chemische Technologie, dritte Folge). Herausgegeben von DR. C. ENGLER, wirkl. geh. Rat und Professor an der Technischen Hochschule Friedericiana in Karlsruhe. IV. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1912. S. xvi + 351. Preis, geh., M. 12; geb., M. 13.50.

The book, as its title states, deals with the properties, occurrence, origin, and methods of finding petroleum and the bitumens rather than with their technology or testing. Particular attention is paid to the geological side, especially to the Hoefer theory of the anticlinal occurrence of petroleum. It may be especially commended to the geologist, the oil-well driller and to any one who desires information about the sub-

ject. It is—particularly the historical part—very interestingly written and apparently no investigator has been overlooked.

It may be cordially commended to those interested in the subject.

A. H. GILL

DIE FABRIKATION DES RUSSES UND DER SCHWARZE aus Abfällen und Nebenprodukten, mit besonderer Berüchsichtigung der Entfärbungskohle. Von DR. HIPPOLYT KÖHLER, Direktor der Rütgerswerke-Aktiengesellschaft, Berlin. Dritte, gänzlich umgearbeitete Auflage. Mit 114 Abbildungen im Text. Neues Handbuch der chemischen Technologie (Bolley's chemische Technologie, dritte Folge), herausgegeben von DR. C. ENGLER, wirkl. geh. Rat und Professor an der Technischen Hochschule Friedericiana in Karlsruhe. V. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1912. S. viii + 228. Preis: geh., M. 7; geb., M. 8.

This book is chiefly a more or less academic description of many different methods of manufacturing commercial soots, which are sold in commerce under the names of "Lamp Black" and "Carbon Black."

We think it is the first serious effort to devote a book to this branch of technical industry, although there are a great number of separate articles on the subject to be found in many technical journals and many popular periodicals, most of which articles, however, have been not only inaccurate, but essentially misleading, giving, in many cases, a totally false and inadequate idea of the processes that they profess to describe.

The present volume is an immense improvement over the best previous sources of information as to this interesting and important industry, which gives us the pigments with which our books and periodicals are printed, as well as the basis of most of the black paint of commerce, not to mention many less important uses for this material.

It does not, however, attain the ideal at which the author aimed, to wit, an entirely correct picture of the present condition of this important industry and for the reason that he is evidently without personal experience of the Carbon Black industry, which is almost the sole basis of black printers' inks in this country and becoming yearly more important in this and other branches in Europe.

His own experience in the manufacture of Lamp Black from tar products gives special value to his observations with regard to this branch of the industry, but a better perspective would be given to the picture as a whole if he had included the statistics of production of Lamp Black and Carbon Black throughout the civilized world and some information as to the actual price to large buyers.

The book begins with a very interesting essay on the phenomena of combustion. The largest part of the book is taken up by a compilation of most of the known and described methods of manufacturing Lamp Black from tar, tar-products, etc., by burning with an insufficient supply of air and permitting the soot to settle on suitable chambers.

The American Carbon Black industry, which produces 25 million pounds a year, is very briefly mentioned; no description whatever is given of the most important methods of manufacture and no suggestion of the relative importance of the different methods.

It is a particularly difficult and thankless task to give a complete and well proportioned account of the industries herein treated, because the capital involved and the number of people interested is so much smaller than in many industries which perhaps for mankind are really of less importance, and, further, because the industry in this country has evolved very different methods from those which are in vogue in Europe, with totally different raw materials and with essentially different finished products.

Therefore, to make a thorough, practical study of the industry would imply wide journeys through many different lands and to comparatively inaccessible spots, much more so than is the case with many chemical industries involving much greater amounts of capital and much greater interest for the technical world.

A study, for instance, of the acid and soda industry in England or Germany or the United States would give a very fair idea of the same industry at any point in the civilized world. The black industry, on the other hand, has developed so differently on the two sides of the Atlantic that it would be necessary to study it in different countries in order to get an equally good and well proportioned conception of the whole.

The author deserves much credit for taking a scientific and general view of a somewhat prosaic industry that has been left too much to so-called practical men, who, relying too much on what the untrained eye can see, often miss the fundamentals of the problems that are confronting them and, therefore, repeat by rote, generation after generation, the same fatuous errors.

The reviewer thinks the book is well worth a careful study by any one engaged in the industries that it describes. He dares to say that there is no person extensively engaged in any of these industries that cannot find in it suggestions that will be of value if intelligently grasped and utilized.

He hopes that the author will some time study the industry in this country and give to the world as intelligent and well proportioned a picture of it as he has of European conditions and he closes this brief review by repeating that he thinks the author has performed a somewhat thankless task incomparably better than any previous writer on the subject.

A careful study of this book will show the fundamental facts, that these commercial soots are all, in the last analysis, either made by the combustion of oily or fatty matter with an insufficient supply of air and the slow settling of the smudge thereby produced or by the direct deposition of the carbon from the flame by contact with relatively cold metallic surfaces or by the superheating of hydrocarbons out of contact with air, and a keen appreciation of these fundamentals will save practical manufacturers much useless experimenting and lead to further progress in the industries involved.

Godfrey L. Cabot

The Iron Ores of Missouri. By G. W. Crane, Missouri Bureau of Geology and Mines. H. A. Buehler, Director. Vol. X, Second Series. Jefferson City, Mo.: Hugh Steffens Printing Co. 1912. pp. xvi + 434.

This book is an excellent report on the iron ores of Missouri, prepared under the direction of the Missouri Bureau of Geology and Mines. It contains an account of the history, development, and production of Missouri iron ores. There is, also, a general discussion of the ores of iron and the factors which control their value. In addition to the general chapters on physiography, geology, and occurrence, distribution and chemical composition of the various types of iron ores, there are descriptions of all the known deposits of the state. The book contains many very good photographs and maps of the different iron-ore regions of Missouri. It contains many interesting facts, and it is to be recommended not only to those interested in mining, but also to those wishing to have at hand a general account of iron ores.

LeRoy McMaster

VOL. XLIX MAY, 1913 No. 5

AMERICAN CHEMICAL JOURNAL

ON THE REACTIONS OF BOTH THE IONS AND THE NONIONIZED FORMS OF ELECTROLYTES[1]

BY S. F. ACREE

[FIFTEENTH[2] COMMUNICATION ON CATALYSIS]

(We are indebted to the Carnegie Institution of Washington for aid in these researches.)

After Arrhenius[3] brought out his theory of the electrolytic dissociation of electrolytes, and Ostwald[4] and Arrhenius and their students found a fairly close agreement between the "strength" of an acid or a base as determined by the conductivity method and by the velocity of the hydrolysis of cane sugar, acetamide, and methyl or ethyl acetate, the opinion gradually grew that electrolytes react through the ionized portions exclusively. In fact, although it was known that *nonionizable* (in the ordinary sense!) substances, such as trialkylamines and alkyl halides, react readily, and the Arrhenius

[1] A lecture delivered before the Chemistry Department of Princeton University on Mar. 7, 1913.

[2] THIS JOURNAL, **27**, 118; **28**, 370; **31**, 185; **32**, 606; **37**, 71, 361; **38**, 1, 258, 489, 746; **39**, 124, 145, 226, 300; **41**, 457, 483; **42**, 115; **43**, 358, 505; **44**, 219; **48**, 352; **49**, 116. Ber. d. chem. Ges., **33**, 1520; **35**, 553; **36**, 3139; **37**, 184, 618; **41**, 3199. Science, **30**, 617 (1909). J. Am. Chem. Soc., **30**, 1755.

[3] Z. physik. Chem., **1**, 631.

[4] J. prakt. Chem., [2] **27**, 1; **28**, 449; **29**, 406; **30**, 231; **31**, 307; **33**, 352; **35**, 112. Z. physik. Chem., **2**, 36, 136, 270.

[5] *Ibid.*, **1**, 110; **2**, 284; **4**, 226; **28**, 217, 326.

theory was criticized by many, especially Kahlenberg[1] and Michael,[2] the theory that all chemical reactions are purely ionic was the one generally accepted up to within the last few years. This belief was probably strengthened greatly by the discovery of the role of simple and complex ions in the electrochemical phenomena so successfully studied in the development of Nernst's[3] theory, and the simple relation existing between the concentration of the ions and the magnitude of the electromotive force observed when a metallic (or gaseous) electrode is immersed in a solution of its ions.

Even in the application of physical chemical conceptions to the study of organic reactions, the very field where the purely ionic theory should have found soil least adapted to its unopposed growth, some of the best workers, Goldschmidt,[4] Bredig,[5] Lapworth,[6] Wegscheider,[7] and Stieglitz,[8] as late as 1908, *did not* apply the conception that *besides* the simple or complex organic ions the *nonionized* portions of the *electrolytes* formed from them are concerned in all catalytic phenomena of organic chemistry in which acids, bases or salts react. However, this new conception of the activity of *nonionized electrolytes* must not be confounded with that involving the activity of *nonelectrolytes*. Thus Stieglitz proved in 1903 that *nonionizable* aminophenyl esters rearrange, acids retarding the reaction catalytically through salt formation, and in particular he proved in 1905 (Dissertation of Schlesinger, Univ. of Chicago) that the nonionized molecules of imido esters decompose in aqueous solutions with characteristic velocity differing most decidedly from the coefficient for their *anions*. But in nearly all of these examples, and others which we have discussed in

[1] J. Phys. Chem., **5**, 339 (1901); **6**, 1 (1902), and subsequent papers in the same journal.

[2] This Journal, **43**, 322.

[3] Z. physik. Chem., **2**, 613; **4**, 129. Wied. Ann., **45**, 360. Nernst's Theoretische Chemie, **1907**, p. 729.

[4] Z. Elektrochem., **15**, 6. Z. physik. Chem., **60**, 728; **70**, 627. Ber. d. chem. Ges., **39**, 711.

[5] Z. Elektrochem., **9**, 118; **10**, 586; **11**, 528; **18**, 535, 539.

[6] J. Chem. Soc., **79**, 1269; **81**, 1503 and 1512; **85**, 31; **91**, 1133; **93**, 30, 85, 2165, 2187. Chem. News, **97**, 248, 309 and 310.

[7] Z. physik. Chem., **39**, 257; **41**, 62, and later articles.

[8] This Journal, **39**, 29, 166, 402, 437, 586, 719. J. Am. Chem. Soc., **32**, 221; **34**, 1687.

various articles, the reactions are due to the activity of *non-electrolytes* and these cases are therefore entirely different from the ones involving *nonionized electrolytes* that we are considering in this paper.

After all it is not difficult to understand in these days of electrons that neutral molecules of either *electrolytes* or *non-electrolytes* can react like the ions. The brilliant ideas of J. J. Thomson[1] and his postulation of "electrostatic induction"[2]

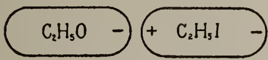


Fig. I

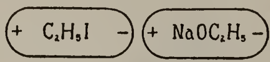


Fig. II.

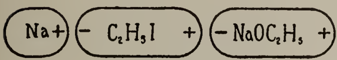


Fig. III.

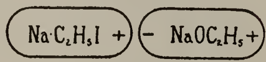


Fig. IV.

may aid us greatly in the study of such reactions. If, in Fig. I, the negative ethylate ion influences a neighboring molecule of ethyl iodide by "electrostatic induction," the particles making up the ethyl iodide molecule must become a "doublet" and rearrange in such a way that the portion nearer the ethylate ion becomes, *in effect*, positive, and therefore capable of attracting the negative ethylate ion as a pith ball is attracted to a charged body. When the ethylate ion and ethyl iodide are drawn together electrically the resulting complex ion can decompose into an iodide ion and ethyl ether.

Now neutral molecules may *at intervals* combine in the same way. A number of colleagues in physics have agreed that through collision or other mechanical disturbance the atomic particles and electrons of the ethyl iodide and sodium ethylate in Fig. II may be so disarranged that a portion of one molecule may become, *in effect*, positive and another portion negative. If the neighboring portions of the two molecules differ elec-

[1] For references to the literature see J. J. Thomson: "The Corpuscular Theory of Matter," pp. 120–141 (1907). L. G. Winston: This Journal, **45**, 547. Acree: *Ibid.*, **48**, 372.

[2] Thomson: *Loc. cit.*, p. 135. Winston: *Loc cit.*

trically, the molecules will be drawn together into a complex structure which can then decompose into sodium iodide and ethyl ether. If the neighboring portions of the two molecules are alike electrically they will be repelled for the moment, to combine afterwards when the conditions are favorable.

Different compounds may vary in the readiness with which they assume the condition favorable for reaction, and hence react with different velocities.

The same ideas may explain to a certain extent the peculiar effect which added salts have on some reactions. The sodium ion in Fig. III may by "induction" charge the ethyl iodide as illustrated, and the sodium ethylate may in turn be influenced by the adjacent positive portion of the ethyl iodide. The ethyl iodide and sodium ethylate therefore attract each other, combine, and then decompose into sodium iodide and ethyl ether. It may well be that many cases of catalysis by acids, bases and salts depend upon this "action at a distance" by the ions, instead of an actual combination illustrated in Fig. IV. We see that it is possible for the sodium ion and ethyl iodide of Fig. III to combine and give the complex cation, sodium-ethyl iodide, illustrated in Fig. IV. This complex cation could then *induce* charges in the sodium ethylate, as illustrated, combine with it and form a complex sodium-sodium ethylate-ethyl iodide compound which decomposes into a sodium ion, sodium iodide and ethyl ether. A negative catalysis would result when the catalyzing ion interferes with the tendency of one of the substances to assume a form favorable for action. To give one of many illustrations, this could happen if the sodium ion attracts toward it, or to it, that portion of the ethyl iodide, for example, which must be adjacent to the sodium ethylate before reaction can proceed.

Many of these changes could be as well explained on Thomson's ideas of "electronic pressure" and the *transfer of electrons* before the actual combination and reaction.

When Brunel and Acree began work in 1905 on the theory that *both the ions and the nonionized molecules must be considered in all reactions of electrolytes* there was already some

evidence from the older work of Arrhenius, Ostwald, Blanksma,[1] van Dam[2] and others that the *nonionized electrolytes* are active in many chemical reactions. In the very tables that Ostwald published to prove the *same activity* of the hydrogen ions of acids in conductivities and in the hydrolysis of cane sugar, methyl acetate, and acetamide, there were many discrepancies larger than experimental errors that caused us to believe that the nonionized acids (and bases) are also concerned in these chemical reactions. The following table[3] shows some cases in which the *activity* of the hydrogen ions is apparently considerably larger in the hydrolysis of methyl acetate and cane sugar than in the conduction of electrons.

Name of acid	Conductivity[4]	Hydrolysis of methyl acetate	Hydrolysis of cane sugar
Acetylformic acid, $CH_3COCOOH$	5.60	6.70	6.49
Trichloroacetic acid, CCl_3COOH	62.3	68.2	75.4
Benzenesulphonic acid, $C_6H_5SO_3H$	74.8	99.0	104.0
Isothionic acid, $C_2H_4(OH)SO_3H$	77.8	98.0	92.0
Ethylsulphonic acid, $C_2H_5SO_3H$	79.9	98.0	91.0
Sulphuric acid, H_2SO_4	65.1	73.9	73.2

All of these examples, and others in which the second and third columns are smaller than the first one, could be interpreted on the basis that *the nonionized acids also show an activity in these chemical reactions.* The greater magnitude of the numbers in Columns 3 and 4, as contrasted with those in Column 2, shows the apparent activity of the nonionized acids (or both ions together), this activity being greater in the hydrolysis of methyl acetate in some cases, but greater in the inversion of cane sugar in other examples, as was predicted from our theory. The trouble with most of this earlier work was

[1] Rec. trav. chim., **21**, 366; **22**, 290.

[2] *Ibid.*, **18**, 408; **19**, 318.

[3] Ostwald's Lehrbuch, **2**, 1, 650. J. prakt. Chem., [2] **30**, 95.

[4] In all of his earlier work Ostwald calculated the per cent. of ionization on the assumption that the value for μ_∞ is the same for all acids (Z. physik. Chem., **1**, 78).

that only one concentration of the catalyzing acid had been used, and we did not have sufficient very acccurate data on the varying concentrations and reaction velocities, and the varying degrees of ionization of the catalyzing acids, to allow us to determine accurately to what extent *both the hydrogen ions and the nonionized acids are catalytically active.* In a few cases, however, the concentration of the acid was varied considerably and Arrhenius[1] and Ostwald[2] recognized from the latter's work that *the rate of inversion of cane sugar is not rigidly proportional to the concentration of the hydrogen ions if the concentration of the acid is rather large.* This deviation was thought by Arrhenius to be similar to other known cases involving a "neutral salt effect."[3] He expressed the rate of inversion in the form $\rho = am + bm^2$, in which ρ is the reaction velocity, m is the concentration of the hydrogen ions, a is a factor which is constant for all acids, and b varies with the acid. This factor bm^2 gave the so-called "salt effect," it having already been shown by Palmaer[4] that in completely ionized solutions of hydrochloric acid the reaction velocity is practically directly proportional to the concentration of the hydrogen ions for a given concentration of sugar. Now the concentration of the sugar was constant[5] in Ostwald's

[1] Z. physik. Chem., **4**, 246. Lehrbuch der Elektrochemie, **1901**, p. 174. See also Lunden: Z. physik. Chem., **49**, 195.

[2] J. prakt. Chem., [2] **31**, 317.

[3] For the literature on salt catalysis see Arrhenius: Z. physik. Chem., **1**, 110; **4**, 226; **31**, 197. Euler: *Ibid.*, **32**, 348. Ber. d. chem. Ges., **39**, 2726. Koelichen: Z. physik. Chem., **33**, 129. Senter: J. Chem. Soc., **91**, 460, and later papers. Reid: This Journal, **21**, 281; **24**, 397; **41**, 483. Spohr: J. prakt. Chem., [2] **32**, 32; **33**, 265. Z. physik. Chem., **2**, 194. Ostwald: J. prakt. Chem., **23**, 219, and papers cited above. Acree and coworkers: This Journal, **38**, 259, 489; **39**, 226; **48**, 352; **49**, 116. Ber. d. chem. Ges., **41**, 3208. Stieglitz and coworkers: This Journal, **39**, 177, 467, 596, 720. J. Am. Chem. Soc., **32**, 221; **34**, 1687.

[4] Z. physik. Chem., **22**, 492.

[5] Ostwald showed (J. prakt. Chem., [2] **31**, 315) that the velocity of hydrolysis varies considerably with the concentration of the sugar, and Cohen (Z. physik. Chem., **23**, 442) and Arrhenius (*Ibid.*, **28**, 319) pointed out that the reaction velocity is proportional to the gas, or osmotic, pressure of the sugar solution. This variation arises from the fact that the concentration of the water, another reacting constituent generally ignored, varies considerably also. It has been shown more accurately recently by the work of Morse and Frazer (This Journal, **34**, 28; **36**, 39; **38**, 175), of Caldwell (Proc. Roy. Soc., London, **74**, 195), *especially* of Rosanoff (J. Am. Chem. Soc., **33**, 1911), of Hudson (*Ibid.*, **30**, 1160; **32**, 885, 889), of Julius Meyer (Z. physik. Chem., **62**, 59; **72**, 117) and others that there is a direct relationship between the osmotic pressure, the mass of sugar per unit mass (kilogram) of water, and the reaction velocity, if all disturbing influences are considered, as Rosanoff has done recently (J. Am. Chem. Soc., **35**, 248).

experiments, and hence there was no change in the effect of the sugar. Inspection shows that the factor bm^2 can therefore be made to represent the *activity of the nonionized acid* (*base or salt*) instead of a "salt effect," and we have already pointed out[1] that all other cases of the so-called "neutral salt effect" may involve the activity of a *nonionized compound.*

If the cane sugar forms with the acid traces of an intermediate salt in the following way:

$$\overset{+}{H} \times C_{12}H_{22}O_{11} = K \times C_{12}H_{22}O_{11}.\overset{+}{H}$$
$$\text{(}C\text{) complex cation}$$

$$\overset{+}{H} \times \overset{-}{Ac} \times C_{12}H_{22}O_{11} = K' \times C_{12}H_{22}O_{11} \times HAc = K'' \times C_{12}H_{22}O_{11}.HAc$$
$$\text{(}N\text{) complex nonionized salt}$$

the reaction velocity can be expressed approximately by the equations

$$\begin{aligned} dx/dt &= aC + bN \\ &= a' \times H \times sugar + b' \times H \times Ac \times sugar \\ (a) \quad &= (a'm + b'm^2) \times sugar \\ (b) \quad &= [a'm + b''(1-m)] \times sugar \end{aligned}$$

which is exactly the form derived by Arrhenius. *We see then that the Arrhenius "salt factor"[2] for these acids may just as well be due to the activity of the nonionized salt of the sugar or to the activity of the nonionized acid.*

The relation between the equations (a) and (b) holds if the ionization of the acid follows the mass law. If such is

[1] THIS JOURNAL, **38**, 273; **41**, 475; **48**, 352; **49**, 116.

[2] Stieglitz first used this Arrhenius idea of a "salt effect" to explain the fact that the rate of hydrolysis of imido ester salts is not strictly proportional to the concentration of the imido ester cations. We pointed out five years ago (THIS JOURNAL, **39**, 521) and showed again, by recalculating his data, in October, 1912 (*Ibid.*, **48**, 370), that he had overlooked the possible activity of the nonionized imido ester salts, and he now (J. Am. Chem. Soc., **34**, 1687, 1689, 1690, 1694) finds that he can reinterpret his results fully as well by recognizing the activity of the nonionized imido ester and bromoamide salts. He has shown that our equations accord excellently with his data. By the use of the data given in his earlier papers, we concluded that there is no appreciable "abnormal salt effect" in his reactions. Although his data were fine for the methods generally in use at that time, the ionizations first published by him are several per cent. in error (cf. THIS JOURNAL, **39**, 729, and J. Am. Chem. Soc., **34**, 1691); on this account the earlier reaction velocities are stated by him (J. Am. Chem. Soc., **34**, 1690, footnote) not to agree with the newer ones. There is therefore an "abnormal salt effect" in his reactions, besides the activity of both the ions and the nonionized salts (J. Am. Chem. Soc., **34**, 1690, 1691, 1694).

not the case, the equation (*b*) holds if the *active*[1] complex cation (*C*) and nonionized salt (*N*) are formed from the hydrogen ions, and nonionized acid, and sugar, or if the reaction velocity is a function of the concentration of the sugar and hydrogen ions and nonionized acid.

Arrhenius did not publish the values which he used for *a* and *b*, but he stated that the value used for *a*, the constant for the *hydrogen ions*, was the same for all acids. As far as we can judge, Arrhenius must have used approximately 31.8 for the value for *a* per gram ion per liter. By the use of some such value he showed that there is a *real* value for *b*, and we have interpreted this as evidence that the nonionized acid is active in all of these cases.

Now the ionization values for strong acids, such as hydrochloric, hydrobromic and nitric acids, *do not* apparently obey the mass law and we must therefore use equation (*b*) to determine whether the *nonionized acids* are active. Dr. Marshall used the data published by Ostwald and found the values

[1] Arrhenius (Z. physik. Chem., **4**, 231; **28**, 317. Rothmund: *Ibid.*, **20**, 168) first advanced this excellent idea that a small portion of the molecules of the changing sugar, ester, etc., are *active* and the others *inactive*. He even went so far as to suggest (*Ibid.*, **28**, 322, footnote) that the *active* molecules may be a combination of the sugar with the water, such as $C_{12}H_{22}O_{11}.H_2O$, for example. He saw also (*Ibid.*, p. 323) the *possibility* that not all H ions are *active*, although stating "Nun sind die Wasserstoffionen warscheinlicherweise vollkommen activ . . Folglich wird jede active Rohrzuckermolekel, welche mit einem Wasserstoffion zusammenstösst, zersetzt werden." It is a strange thing that Arrhenius never seemed to *combine* the idea of the *activity of all H ions from acids* with the idea of active cane sugar molecules by assuming a *union* of the *active* H ions with cane sugar or cane sugar and water together, and the formation of an *active complex cation, or system*, $C_{12}H_{22}O_{11}.\overset{+}{H} + H_2O$ or $H_2O.C_{12}H_{22}O_{11}.\overset{+}{H}$, which yields the end products. Arrhenius assumed the *cane sugar molecules* to be *active*, whereas to-day the leaders in catalysis believe that the combined *sugar-water-hydrogen ion complexes* are the *active* molecules, an idea evolved from the discovery of the basic properties of oxygen by Collie and Tickle (J. Chem. Soc., **75**, 710) and Baeyer and Villiger (Ber. d. chem. Ges., **34**, 2692; **35**, 1201). Both ideas lead to practically the same results, kinetically, in those cases involving only a trace of active salt, but the later hypothesis is the only one tenable when considerable amounts of the *intermediate active compound* are present. Bredig first suggested *in a footnote*, as a result of his study of the catalytic decomposition of hydrogen peroxide by iodides, (Z. Elektrochem., **9**, 118), that in the catalysis of esters and cane sugar by acids the hydrogen ions combine with the ester or cane sugar and form an intermediate complex *oxonium cation* which is then hydrolyzed. See Stieglitz (Congress Arts and Sciences, St. Louis, 1904, and later papers), where, as a result of his very fine work on imido ester salts, the relation of intermediate *oxonium cation* formation to catalysis received its first full quantitative interpretation in a way to agree with the main facts of the catalysis of esters. See also later work by Bredig on this subject (Z. Electrochem., **10**, 582; **11**, 528. Z. physik. Chem., **47**, 185; **60**, 202). They both overlooked, however, the activity of the *nonionized salts*, which was brought out first by Acree and Johnson (This Journal, **37**, 410; **38**, 258).

$K_i = 31.2$ and $K_m = 83.8$ for hydrochloric acid, $K_i = 31.4$ and $K_m = 93.4$ for hydrobromic acid, and $K_i = 31.4$ and $K_m = 73.1$ for nitric acid. *These give us nearly the same values for K_i for the hydrogen ion from all three acids*, as we should get, and show furthermore that K_m, *the activity of the nonionized acid, or nonionized sugar salt, is from 2 to 3 times that of the hydrogen ions*. By the use of the best values we get $K_i = 30.9$, 30.6 and 30.8, respectively, for the hydrogen ion, which are as close to the above as the errors permit. By the use of the values of K_i and K_m given above, Dr. Marshall recalculated the values for K_n and we give the results in the following tables:

Hydrochloric Acid and Sugar

$K_i = 31.2 \quad K_n = 83.8$

Conc. of acid	α	K_m found	K_n calc.
0.5 N	0.809	41.0	41.2
0.1 N	0.953	33.4	33.7
0.01 N	1.000	31.3	31.2

Hydrobromic Acid and Sugar

$K_i = 31.4 \quad K_m = 93.4$

Conc. of acid	α	K_n found	K_n calc.
0.5 N	0.805	44.7	43.5
0.1 N	0.951	34.1	34.4
0.01 N	1.000	31.8	31.4

Nitric Acid and Sugar

$K_i = 31.4 \quad K_m = 73.1$

Conc. of acid	α	K_n found	K_n calc.
0.5 *N*	0.811	40.2	39.3
0.1 N	0.953	33.1	33.4
0.01 N	1.000	31.7	31.4

The agreement between the calculated and found values is just as good as Arrhenius published and shows that we can fully as well interpret the results as proving that *the nonionized acid, or nonionized sugar salt, enters into the reaction to a much greater extent than does the hydrogen ion.* Both the reaction velocities and ionizations published by Ostwald, although fine for their day, could be improved and we should expect to

secure better concordance with better experimental data. There is no necessity for discussing these details further here.

We have furthermore made some calculations by applying Equation (*b*) to the results obtained by Ostwald with the organic acids (formic, acetic, propionic, butyric and succinic) and have found a *very small activity* for the nonionized organic acids. We consider these results of Ostwald for the organic acids to be less reliable than those obtained by the use of the stronger acids, and hence do not reproduce our data here (see p. 355).

In the same article referred to above Arrhenius[1] studied the effect of salts as well as nonelectrolytes (*Nichtleitern!*) on the inversion of cane sugar by hydrochloric and nitric acids by using various salts and methyl alcohol, ethyl alcohol, acetone, mercuric chloride, and *the nonionized forms of the organic acids.* When he added varying concentrations of the alcohols, acetone and organic acids to 0.005 N and 0.05 N hydrochloric acid and to 0.05 N nitric acid, he found that the alcohols had practically no effect but that *the nonionized forms of formic, succinic, acetic, propionic and butyric acids in every case increase the reaction velocity above the calculated amount.* Now we have interpreted this so-called "effect of these nonelectrolytes" as chiefly the catalytic activity of the nonionized organic acids or of the nonionized salt of the sugar discussed above (see page 351, Equations (*a*) and (*b*)), the alcohol naturally having no such activity. The total change observed may be due partially to a real "abnormal salt effect," resulting from changes in the physical properties of the solutions and to other causes. Arrhenius calculated that one gram molecule each of nonionized formic, succinic, acetic, propionic and butyric acids increases the activity of 0.05 N nitric acid by the amounts represented by 13.2, 9.9, 11.7, 9.2 and 6.7, the activity of the 0.05 N nitric acid being represented by 29.8 at 39°.3.

If we assume, from Arrhenius' data, that the activity of a gram of hydrogen ions per liter is at least 20 × 29.8, or roughly 600, we see that the activity of these nonionized organic acids

[1] Z. physik. Chem., 4, 239.

is *far smaller* than that of the hydrogen ion and still smaller than that of the nonionized hydrochloric, hydrobromic and nitric acids, which is exactly the conclusion reached above from the consideration of Ostwald's work (see p. 354). We see, furthermore, that the activity of the series of nonionized monobasic organic acids given in this list is closely parallel to the affinity constants. We call especial attention to this fact[1] that the *nonionized forms* of the *weak* (organic) *acids* have apparently *much smaller* activities than the nonionized forms of the *strong acids*. While we do not place so much reliance on *our purely approximate* recalculation of the data of Ostwald and Arrhenius, we have found in *all* of *our* work, with one or two apparent exceptions, that the activity of *every alkyl halide, or nitrile*, with the nonionized ethylates and phenolates increases uniformly as we go from the weaker to the stronger electrolyte. Since we look upon the ethylates *as bases in alcohol*, and we have found that Koelichen's work seems to show that nonionized barium hydroxide is less active than the nonionized form of a stronger base, sodium hydroxide, it may be found later to be a general rule that in a given series of reactions the activity of the nonionized form is a function of the affinity constant of the given acid, base or salt. This fact will be found of great importance, probably, in the study of energy changes, whereby even the exceptions may be brought into harmony with the more general rule.

Ostwald,[2] Arrhenius,[3] Spohr,[4] Warder,[5] and Reicher[6] studied the rate of saponification of various esters of acetic acid by weak and strong bases, and both Ostwald and Arrhenius showed that there was excellent agreement between the concentration of the hydroxyl ions, whatever the nature of the base, and the rate of saponification of the ester. This work and that of Osaka,[7] of Bredig and Will,[8] as well as that of

[1] Bredig: Z. Elektrochem., **18**, 543.
[2] J. prakt. Chem., [2] **35**, 112.
[3] Z. physik. Chem., **1**, 110; **2**, 290.
[4] *Ibid.*, **2**, 194.
[5] This Journal, **3**, 203, 294, 340. Ber. d. chem. Ges., **14**, 1361.
[6] Ann. Chem. (Liebig), **228**, 257.
[7] Z. physik. Chem., **35**, 661.
[8] Ber. d. chem. Ges., **21**, 2777; see also Gazz. chim. ital., **30**, II, 476.

Koelichen,[1] discussed below, had such a profound influence on chemists that nearly every one to-day believes that all bases react through their hydroxyl ions alone. This belief has probably been greatly strengthened by the electrochemical work involving the relation between the electromotive force and the concentration of the hydroxyl ions.[2] Even though it may be true that the saponification of many esters takes place through the activity of the hydroxyl ions, and does not appreciably involve the nonionized bases, it does not follow that *all* reactions of bases involve *only* the hydroxyl ions. This is well illustrated by the following example which shows that the purely ionic conception of reactions perhaps misled Ostwald in the interpretation of some of the studies carried out in his laboratory.

At Ostwald's suggestion, Koelichen made a beautiful study of the reversible condensation of acetone by alkalis into diacetone alcohol, and they interpreted their results on Ostwald's idea that only the hydroxyl ions are catalytically active. A close inspection of their work shows that their reaction velocities were uniformly larger than those calculated from Ostwald's idea that only the hydroxyl ions are active, and really prove that *both sodium hydroxide and barium hydroxide react through both their hydroxyl ions and the nonionized bases.* In the following tables we give a recalculation of their data by the use of our equations and the values $K_i = 0.2315$ and $K_m = 0.2315$ for sodium hydroxide and $K_i = 0.232$ and $K_m = 0.150$ for barium hydroxide. These approximations seem to show that the hydroxyl ion shows the same activity per gram ion in both cases, but that nonionized barium hydroxide is *less active* in this case than is nonionized sodium hydroxide. The use of our theory and equations gives values (K_v' calc.) involving uniformly smaller experimental errors than those (K_v calc.) calculated by the use of Ostwald's theory, as the following tables show:

[1] Z. physik. Chem., **33**, 129.

[2] Lorenz and Böhi: Z. physik. Chem., **66**, 733. Lewis: *Ibid.*, **55**, 449. Brönsted: *Ibid.*, **65**, 84. For a fine collection of the literature see Abegg, Auerbach, und Luther: "Messungen elektromotorischer Kräfte galvanischer Ketten, **1911**."

Sodium Hydroxide and Diacetone Alcohol

$K_i = 0.2315 \quad K_m = 0.2315$

Conc. of NaOH	0.0942	0.0471	0.01884	0.00942	0.00471	(0.002355)
α	0.92	0.956	0.977	0.986	0.995	(1.000)
K_v found	0.02181	0.01110	0.004372	0.002222	0.001053	(0.000445)
K_v calc.	(0.02181)	0.001121	0.004585	0.002313	0.001166	(0.000586)
Error in per cent.	0.00	—0.99	—4.64	—4.10	—10.73	(—31.70)
K_v' calc.	0.02181	0.01090	0.004361	0.002181	0.001090	(0.000545)
Error in per cent.	0.00	+1.8	+0.25	+1.8	—3.5	(—19.0)

Barium Hydroxide and Diacetone Alcohol

$K_i = 0.232 \quad K_m = 0.150$

Conc. of $Ba(OH)_2$	0.0942	0.0471	0.01884	0.00942	0.00471
α	0.85	0.89	0.94	0.975	0.99
K_v found	0.02036	0.01083	0.004226	0.002168	0.001061
Error in per cent.	+2.1	+3.8	—4.15	—5.2	—8.6
K_v' calc.	0.02072	0.01050	0.004277	0.002167	0.001088
Error in per cent.	—1.71	+3.1	—1.2	+0.06	—2.5

These tables, and our reinterpretation of the work of Stieglitz and Schlesinger on the decomposition of imido esters by barium hydroxide, discussed in the next article on page 372, show very clearly that the *possibility* of the reaction of the *nonionized bases* should be considered in all such cases.[1]

Then, too, the work of Blanksma[2] on the rearrangement of acetylchloroaminobenzene in the presence of hydrochloric acid showed that the reaction velocity *is not* proportional to the concentration of the hydrogen ions, or complex cations, as was assumed by Arrhenius and Ostwald to be the case in practically all of the studies published then on "the[3] hydrolysis of such weak bases as esters, amides, amidines, oximes" and in "the formation and saponification of esters, and the hydrolysis of acetamide,"

$$CH_3CONClC_6H_5 + \overset{+}{H} \rightleftarrows \underset{\text{cation not appreciably active}}{\overset{+}{CH_3CONHClC_6H_5}} \longrightarrow CH_3CONHC_6H_4Cl + \overset{+}{H}$$

$$CH_3COOCH_3 + \overset{+}{H} + H_2O \rightleftarrows \underset{\text{cation chief substance transformed}}{CH_3COOCH_3.\overset{+}{H}} + H_2O \longrightarrow CH_3COOH + \overset{+}{H} + CH_3OH$$

but that the reaction velocity *is* nearly proportional to the *square* of the concentration of the hydrogen ions, or product of the concentrations of the hydrogen and chloride ions, and hence, *on our interpretation*, to the concentration of the *nonionized salt* formed by the union of the acetylchloroaminobenzene with *both ions*, or the nonionized acid, as follows:

$$CH_3CONClC_6H_5 + \overset{+}{H} + \overset{-}{Cl} \rightleftarrows \underset{\text{nonionized salt}}{CH_3CONHCl_2C_6H_5} \longrightarrow CH_3CONHC_6H_4Cl + \overset{+}{H} + \overset{-}{Cl}$$

This interpretation was fully justified by later work in 1906–7 by Johnson[4] and Acree on the action of hydrochloric and hydro-

[1] Regarding the possible activity of the ions and molecules of sulphydrates, which are analogous to hydroxides, see the next article, THIS JOURNAL, **49**, 371.

[2] *Loc. cit.*

[3] Johnson and Acree: THIS JOURNAL, **37**, 411, 412.

[4] *Ibid.*, **37**, 410; **48**, 358.

bromic acids on acetylchloroaminobenzene and acetylbromoaminobenzene.

The work of van Dam[1] showed us clearly that in the rearrangement of benzbromoamide by alkalies *both* the *ions* and the *nonionized salt* are transformed into the end products, as discussed in a former communication.[2] Van Dam had interpreted his studies[3] as a pure catalysis by the hydroxyl ions alone.

$$C_6H_5CONBrH + KOH \longrightarrow \begin{cases} \left.\begin{matrix} C_6H_5CO\overline{N}Br \\ \text{and} \\ C_6H_5C(\overline{O}):NBr \end{matrix}\right\} \longrightarrow C_6H_5N:C:O + \overline{Br} \\ \left.\begin{matrix} C_6H_5CONKBr \\ \text{and} \\ C_6H_5C(OK):NBr \end{matrix}\right\} \longrightarrow C_6H_5N:C:O + KBr \end{cases}$$

Goldschmidt[4] found that the rate of change of diazoaminobenzene in aniline is directly proportional to the concentration of the added aniline hydrochloride. We interpreted this reaction in 1907[5] and again recently[6] as, at least partially, a reaction of the nonionized hydrochloride of the diazoaminobenzene analogous to the rearrangement of acetylchloroaminobenzene by hydrochloric acid,

$$(C_6H_5NH_2.HCl + C_6H_5N:NNHC_6H_5 \rightleftarrows C_6H_5N:NNH_2ClC_6H_5 + C_6H_5NH_2) \longrightarrow C_6H_5N:NC_6H_4NH_2.HCl$$

In 1905 Bredig and Stern[7] published a quantitative study of the condensation of benzaldehyde into benzoin by cyanides, which they interpreted as a *pure* catalysis of the cyanide ions.

[1] Rec. trav. chim., **18**, 408; **19**, 318.

[2] Acree: This Journal, **48**, 358.

[3] Stieglitz later (Ber. d. chem. Ges., **43**, 783) began an investigation along this same line to see "ob nicht etwa *nur das Ion* umlagerungsfähig ist" (italics ours!) but has recently (J. Am. Chem. Soc., **34**, 1688) come to the conclusion that *both the ions* and the *nonionized salt* rearrange, as we had pointed out at the Boston meeting of the A. A. A. S. in 1909 and again recently (This Journal, **48**, 358).

[4] Ber. d. chem. Ges., **21**, 1016, 2557; **25**, 1347; **29**, 1369, 1899. Z. physik. Chem., **29**, 89; **70**, 627. Ann. Chem. (Liebig), **351**, 108.

[5] This Journal, **39**, 523, lines 20–21. Goldschmidt has since then (Z. physik. Chem., **70**, 643) interpreted the reaction as one involving the *nonionized* aniline hydrochloride.

[6] This Journal, **48**, 368.

[7] Z. Elektrochem., **10**, 582.

alone.[1] *They assumed a constant per cent. of ionization* for 66 per cent. alcoholic solutions of potassium cyanide varying from 0.4 N to 0.05 N. This assumption is, of course, extremely improbable, as the ionization increases very greatly in such a case.

Since their reaction velocities, per gram molecule of potassium cyanide, did not increase noticeably with increasing ionization, we[2] have been able to show that their results really harmonize with our theory that *the cyanide ions and the nonionized potassium cyanide are, in this case, equally active, and that K_i and K_m are about 0.089.*

$$2C_6H_5CHO + \overline{CN} \longrightarrow C_6H_5COCH(OH)C_6H_5 + \overline{CN}$$
$$2C_6H_5CHO + KCN \longrightarrow C_6H_5COCH(OH)C_6H_5 + KCN$$

In 1905 Tubandt[3] published a fine study of the catalytic reversible inversion of *d*- and *l*-menthones by sodium ethylate, which he did not interpret in terms of the ionization theory. We have shown[4] that his work harmonizes excellently with our theory and that *both the ethylate ions and the nonionized sodium ethylate* invert the menthone with the same velocity; namely, 0.41 at 20° and 0.93 at 30° for each gram ion or molecule per liter.

These were the chief organic[5] reactions with which we were familiar in 1905 and which *seemed* to involve both the ions and the nonionized forms of acids, bases or salts. These reactions showed, to say the least, a *deviation* from a purely ionic reaction, which Arrhenius and others interpreted as a "salt effect," but which we interpreted as *partially*, at least, an

[1] Bredig and Walton (Z. Elektrochem., **9**, 114. Z. physik. Chem., **47**, 185) showed in a very pretty study that sodium, potassium and ammonium iodides cause the pure *catalysis* of hydrogen peroxide with a velocity which is nearly proportional to the concentration of the *iodide ions*. Since cadmium iodide decomposes hydrogen peroxide more rapidly than they calculated from their theory, the writer suggests that the *cadmium iodide molecules* may be active. Unfortunately not enough is now known concerning the ionization of such ternary electrolytes.

[2] This Journal, **48**, 380.

[3] Ann. Chem. (Liebig), **339**, 41; **354**, 259; **377**, 284.

[4] This Journal, **48**, 379.

[5] We have noted a number of *inorganic* reactions, oxidations, reductions, etc., which seem to involve both ions and nonionized electrolytes, and we shall discuss these later in a special article.

actual activity of the nonionized substances. In April,[1] 1907, and September,[2] 1907, we published a preliminary report introducing the theory that *both*[3] *ions and nonionized salts, acids and bases must be considered in all reactions*, and have since then been steadily at work on this theory. We realized at that time the seriousness of our assumption, an assumption made in the face of such eminent men, and for that reason we did not care to reinterpret their work then. We preferred to work out a number of different reactions very accurately and establish the idea firmly on an experimental basis. Perhaps because of its very novelty the idea has been considered and passed over by many others. Even after we published our first report with some experimental evidence others perhaps questioned the theory and failed to use it, but have gradually come to the same idea, as the following examples illustrate.

Lapworth wrote me recently as follows: "At the time I read your first catalysis paper, and controversy with Stieglitz, this considerable advance on the theoretical side made by you must have made no lasting impression on me, in spite of the fact that Stieglitz acknowledged the fact it was novel. Perhaps *because* of its novelty I dismissed it too hastily in reading."

Stieglitz has pointed out in letters and in his publications[4] that he overlooked at first the importance of the suggestion. This is shown by the fact that after we *emphasized*[5] *71 times*, in equations and formulas and words, in one article alone, the activity of the nonionized electrolytes in 1907, he published a number of very fine papers[6] in 1908 interpreting his work on imido ester salts as reactions of ions alone and has only recently,[7] after we pointed out the possibility of the activity of his non-

[1] This Journal, **37**, 410.

[2] *Ibid.*, **38**, 258.

[3] We included "acids, bases and salts" in 1907 in the above articles and This Journal, **39**, 155, 226, and many other places in which we pointed out that *pure* catalysis and *pseudo* catalysis are fundamentally alike, but we have confined our attention chiefly to the reactions of the bases and salts.

[4] *Ibid.*, **39**, 402, 403.

[5] In *Ibid.*, **38**, 258, and many other articles.

[6] This Journal, **39**, 177, 467, 596, 720. J. Am. Chem. Soc., **32**, 221.

[7] *Ibid.*, **34**, 1687, 1688, 1689, 1690, 1694.

ionized[1] salts, come to realize that he can give a better reinterpretation of his imido ester reactions and the Beckmann rearrangement by recognizing the activity of the nonionized salts.

In 1908 Goldschmidt[2] wrote a discussion of our work on the action of the alkyl halides on the urazole salts,[3] but considered only the ions. Although our articles to which he referred (1907–8) contained full discussions of the activity of the *nonionized salts*, Goldschmidt apparently neglected this fact and it was not till 1909–10 that he at last fully realized the importance of the idea and began[4] to use it to reinterpret his own work.

In his very complete and thoughtful review of catalysis in 1909, Bodenstein[5] discussed our idea that ions may react but failed entirely to mention the nonionized salts. This is all the more noticeable when we consider the fact that he discussed, on page 412, the rearrangement of acetylchloroaminobenzene, the very reaction which we emphasized in this connection.

In 1908 Bredig wrote me several letters dealing with catalysis, discussing in particular our theory that the nonionized salt of acetylchloroaminobenzene rearranges. He raised the objection that in such cases the really *active* system may be *base* + *H* + *Cl* instead of the nonionized salt, *base.HCl*, and did not believe that we can tell whether the nonionized salt, or both the ions together, undergoes transformation. He has now, however, come to the other point of view and is now[6] using the same theory and equations[7] to reinterpret his reactions of acids and diazoacetic ester. He formerly[8] thought that only the hydrogen ions act catalytically, but he now

[1] This Journal, **39**, 521; **48**, 371.

[2] Z. Elektrochem., **15**, 10.

[3] Ber. d. chem. Ges., **41**, 3206, 3210, 3211, 3213, 3214. This Journal, **37**, 410; **38**, 258, 489.

[4] Z. Elektrochem., **15**, 6. Z. physik. Chem., **70**, 627.

[5] Z. Elektrochem., **15**, 390.

[6] Bredig: *Ibid.*, **18**, 535, 543.

[7] Cf. Brunel and Acree: This Journal, **43**, 519 (1910), and Bredig and Snethloge: Z. Elektrochem., **18**, 540 (1912).

[8] Bredig and Fraenkel: *Ibid.*, **11**, 525 (1905); Z. physik. Chem., **60**, 202 (1907).

believes that *both* the *hydrogen ions* and the *nonionized acid* are active.

A number of articles have been published recently by Senter,[1] Holmberg,[2] Rivett,[3] and others which seem to involve nonionized salts. Deserving of especial attention is an article by L. W. Jones on the Beckmann rearrangement,[4] the treatment of which shows the thoughtful care and fine spirit back of all his work. In the last year H. C. Biddle[5] has shown that nonionized acids are active in a number of important reactions involving alkaloids and dyes. In the field of enzyme work, Hudson[6] has shown in a number of important papers the effect of hydrogen ions and hydroxyl ions on the activity of invertase and emulsin.

When we proposed the theory of the activity of both ions and nonionized electrolytes we saw that much more work was needed involving *very accurate measurements* of (1) the *reaction velocities*, of (2) the *true ionization* of the reacting electrolytes and of (3) the so-called "salt effect"[7] which had been noticed in a number of cases by Arrhenius, Euler, Spohr and others. Since a large change in the per cent. of ionization is absolutely necessary in order to allow us to measure *most accurately* the activity of the ions and of the nonionized substances, we chose ethyl and methyl alcohols as the chief solvents for our work. There is a far greater change in ionization in ethyl alcohol, as we go from N/1 to N/1000 solutions, than is the case in aqueous solutions. The work in our laboratory has now shown that in a number of cases we seem beyond doubt to be dealing with the reactions of both ions and nonionized electrolytes in both concentrated and dilute solutions, so we shall begin now to publish in about twenty articles the preliminary portion of the work and shall make the final corrections of our constants

[1] J. Chem. Soc., **91**, 460; **95**, 1827; **97**, 346; **99**, 95; **101**, 2528, 2534. Ber. d. chem. Ges., **45**, 2318.

[2] Z. physik. Chem., **79**, 147, 621. Ber. d. chem. Ges., **45**, 3000.

[3] Z. physik. Chem., **82**, 201.

[4] THIS JOURNAL, **48**, 1.

[5] Ber. d. Chem. Ges., **45**, 526, 2832. J. Am. Chem. Soc., **34**, 500; **35**, 273.

[6] J. Am. Chem. Soc., **30**, 1160, 1564; **31**, 655, 1136, 1242; **32**, 774, 1220, and later papers.

[7] For references see p. 350.

later when we study the effects of fluidity, solvation, complex salt formation, and other uncertain physical factors.

In order to bring up to date the evidence which we have obtained I give a few tables of some of the constants obtained by my various coworkers. If both the ethylate ions and the nonionized portions of sodium, potassium and lithium ethylates react with alkyl halides as follows:

$$\overline{O}C_2H_5 + C_2H_5I \rightleftarrows C_2H_5\underset{I}{\overline{O}}C_2H_5 \longrightarrow (C_2H_5)_2O + \overline{I}$$

$$NaOC_2H_5 + C_2H_5I \rightleftarrows C_2H_5\underset{I}{\overset{Na}{O}}C_2H_5 \longrightarrow (C_2H_5)_2O + NaI$$

and the results are analyzed by means of the equation[1]

$$dx/dt = [K_i\alpha + K_m(1 - \alpha)]\,(C_{salt} - x) \times (C_{alkyl\ halide} - x)\,(1 + (f)\,C_{salt}),$$

we should find the same values for K_i, the activity of a gram equivalent of ethylate ions with a certain alkyl halide, whether we use sodium, potassium or lithium ethylate. Of course, the values of K_m, the activity of a gram equivalent of the nonionized ethylate salt, would vary, because the nonionized molecules of sodium, potassium and lithium ethylates are different. The theory[2] has been fully substantiated by the work of Dr. Julia P. Harrison, Dr. E. K. Marshall, Jr., and Mr. J. H. Shrader on the action of ethyl bromide on sodium, potassium and lithium ethylates in solutions varying from N/1 to N/32. The conductivities and ionization of all the following salts at 0°, 25°, and 35° were measured by Dr. H. C. Robertson, Jr.:

	K_i	K_m
Dr. Marshall: Sodium ethylate and ethyl bromide	0.00576	0.00233
Dr. Harrison: The same	0.00557	0.00232
Dr. Harrison: Potassium ethylate and ethyl bromide	0.0055	0.0029
Mr. Shrader: Lithium ethylate and ethyl bromide	0.0057	0.00157

[1] For the development and use of these equations, see especially This Journal, **37**, 410; **38**, 258; **43**, 519; **48**, 353.

[2] For a preliminary report of part of the following work, see This Journal, **48**, 352.

Although the reaction velocities and ionizations of these three salts vary widely, these values of K_i are identical within the experimental errors, as they should be. But the values of K_m for the nonionized sodium, potassium and lithium ethylates vary widely, in accordance with our theory. *The activity of the nonionized salts* is from 30 per cent. to 55 per cent. of that of the ethylate ion.

Similar evidence has been obtained by Dr. Marshall, Dr. Harrison and Mr. Shrader in the study of the action of ethyl iodide on sodium, potassium and lithium ethylates.

	K_i	K_m
Dr. Marshall: Sodium ethylate and ethyl iodide	0.0120	0.00427
Mr. Shrader: The same	0.0122	0.0040
Dr. Harrison: Potassium ethylate and ethyl iodide	0.0121	0.0047
Mr. Shrader: Lithium ethylate and ethyl iodide	0.01215	0.0030

The reaction velocities and ionization of these salts vary widely, but the values for K_i for the ethylate ion and ethyl iodide are practically the same for all three ethylates, as they should be. The values for K_m for the *nonionized ethylates vary* from 25 per cent. to 38 per cent. of the value of K_i, in accordance with the theory.

The same kind of proof has been obtained by Dr. H. C. Robertson, Jr., Dr. Harrison and Miss B. Marion Brown in their studies of the reactions of methyl iodide with sodium and potassium ethylates.

	K_i	K_m
Dr. Robertson: Sodium ethylate and methyl iodide	0.127	0.0589
Miss Brown: The same	0.127	0.0594
Dr. Harrison: Potassium ethylate and methyl iodide	0.1264	0.0676

The theory is substantiated fully as well here as in the other studies, and Miss Brown is continuing these investigations at 0° and 35°.

	K_i	K_m
Miss Brown: Sodium ethylate and methyl iodide at 0°	0.0049	0.0030
Miss Brown: Lithium ethylate and methyl iodide at 0°	0.0052	0.0020
Miss Brown: Potassium ethylate and methyl iodide at 0°	0.0053	0.0034

Dr. Robertson and Mr. J. H. Shrader have obtained excellent evidence that methyl iodide, ethyl iodide and allyl bromide react at 25° and 35° with *both the ions and nonionized portions of sodium, potassium and lithium phenolates.*

	K_i	K_m
Dr. Robertson: Sodium phenolate and methyl iodide at 25°	0.0282	0.0047
Mr. Shrader: Potassium phenolate and methyl iodide at 25°	0.0283	0.0037
Mr. Shrader: Lithium phenolate and methyl iodide at 25°	0.0284	0.0040
Dr. Robertson: Sodium phenolate and methyl iodide at 35°	0.091	0.0131
Dr. Robertson: Sodium phenolate and ethyl iodide at 25°	0.0056	0.00099
Mr. Shrader: Potassium phenolate and ethyl iodide at 25°	0.0052	0.00101
Mr. Shrader: Lithium phenolate and ethyl iodide at 25°	0.00534	0.00091
Dr. Robertson: Sodium phenolate and ethyl iodide at 35°	0.0184	0.00323
Mr. Shrader: Potassium phenolate and ethyl iodide at 35°	0.0197	0.0027
Mr. Shrader: Lithium phenolate and ethyl iodide at 35°	0.0174	0.0032

The values of K_i for the reaction of methyl iodide with sodium, potassium and lithium phenolates at 25°, and of K_i for ethyl iodide with sodium, potassium and lithium phenolates at 25° and 35°, are identical within the experimental errors. The values of K_m for the nonionized salts vary, in accordance with the theory. It will be observed that the ratios $K_i : K_m$ for the phenolates vary from 5 to 7 and are much larger than the ratios $K_i : K_m$ for the ethylates.

In other articles[1] it was pointed out that Dr. F. M. Rogers and Dr. Sidney Nirdlinger found in 1908 that *ethyl iodide reacts at 25° with both the anion and the nonionized form of sodium 1-phenyl-3-thiourazole.* They obtained the values $K_i = 0.435$ and $K_m = 0.17$. Dr. Joseph Chandler has repeated their work under somewhat better conditions and obtained the values $K_i = 0.465$ and $K_m = 0.16$, which are in substantial agreement with the above.

Dr. E. K. Marshall and Dr. Julia P. Harrison have shown that sodium, potassium and lithium ethylates cause the reversible change of acetimido ethyl ester and benzimido ethyl ester into the corresponding nitriles and ethyl alcohol. *The ethylate ions and nonionized sodium ethylate are both catalytically active.* For acetimido ethyl ester and sodium ethylate Dr. Marshall finds the values $K_i = 0.344$ and $K_m = 0.228$, while for benzimido ethyl ester Dr. Harrison finds the values $K_i = 0.1172$ and $K_m = 0.0976$. The experimental work forms the basis of the following article.

In all of the above studies the concentrations were varied from N/1 to N/32 or N/64, but these solutions cannot be considered *ideal.* Dr. C. N. Myers has therefore undertaken the study of the reversible addition of ethyl alcohol to *p*-bromobenzonitrile, and the catalytic effect of sodium, potassium and lithium ethylates in solutions as dilute as N/2048. He finds that our theory holds excellently in these *ideal solutions* (N/32 to N/2048) and he obtains the rounded values $K_i = 0.160$ and $K_m = 0.160$ for sodium ethylate, $K_i = 0.160$ and $K_m = 0.141$ for potassium ethylate, and $K_i = 0.161$ and $K_m = 0.087$ for lithium ethylate. In the N/32 solutions the sodium ethylate reacts 50 per cent. faster than does the lithium ethylate, because the sodium ethylate is more highly ionized and the ethylate ions and nonionized sodium ethylate molecules react faster than do the nonionized lithium ethylate molecules. But all three salts are practically completely ionized in the N/2048 solutions, in which the concentrations of the ethylate ions are therefore practically alike. Hence these three salts should show, and actually do have, the same activity in these dilute

[1] This Journal, **43**, 519, 551; **49**, 116.

(N/2048) solutions. The work on the tetramethyl ammonium ethylate, $(CH_3)_4\overset{+}{N}\overset{-}{O}C_2H_5$ is in progress, and agrees in the main with these ideas, and the preliminary work on thallium ethylate shows it to be much less active than even the lithium ethylate, in accordance with the theory.

It is thus seen that our theory of the activity of *both ions and nonionized electrolytes seems to hold in both concentrated and ideal solutions.* We realize (1) that our values for K_i and K_m for the concentrated solutions contain a small "abnormal salt effect" in some cases, (2) that the abnormal fluidity of the solutions, complex ions and salts, and the solvation of the electrolytes make the value $\mu_v : \mu_\infty$ an inaccurate measure of the per cent. of ionization, and (3) that the abnormal physical properties of these solutions may influence all of the data. These effects, however, are much the same for solutions of similar concentrations with all of these ethylates, phenolates, etc., and the values for K_i and K_m for corresponding sodium, potassium and lithium salts will doubtless be changed very much alike. We are studying all of these reactions in the *ideal solutions*, and are measuring the physical factors, just as rapidly as possible, and shall make the final corrections later in our completed articles.

It is therefore clear that all of our work and our reinterpretation of the work of Arrhenius, Ostwald, Bredig, Goldschmidt, Stieglitz, Blanksma, van Dam, and others, gives evidence that *both ions and nonionized electrolytes, and nonionizable substances, may be concerned in all chemical reactions.* In so far as the activity of the *ions* is proven in our work we have brought new evidence to place Arrhenius' brilliant theory of ionization, and Ostwald's conception of the activity of ions, on a more secure basis. In so far as the activity of the *nonionized electrolytes* is established we have added evidence to the newer theory. But all of this is merely a beginning. In order to learn how and why chemical reactions take place we must look far deeper than the mass law and the theory of electrons, down into the changes of energy within the atoms and molecules.

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ON THE REACTIONS OF BOTH THE IONS AND THE NONIONIZED FORMS OF ELECTROLYTES

THE REVERSIBLE ADDITION OF ALCOHOLS TO NITRILES CATALYZED BY SODIUM ETHYLATE, II

By E. K. Marshall, Jr., Julia Peachy Harrison and S. F. Acree

[SIXTEENTH COMMUNICATION ON CATALYSIS]

(We are indebted to the Carnegie Institution of Washington for aid in these researches.)

Sodium ethylate has long been used as a catalyzer[1] in the inversion of menthone, in the acetoacetic ester synthesis and allied reactions, in the study of the reactions of alcohols with nitriles[2] by Nef, Stieglitz and Dains, and especially Stieglitz and McKee, and McKee, and of alcohols with mustard oils, acid chlorides, alkyl halides and in many other cases. The *quantitative* study of the mechanism of these reactions is of the greatest importance not only to the organic chemist but to all other chemists. In connection with other investigations along these lines we have taken up the *quantitative*[3] study of the addition of alcohols to nitriles in order (1) to learn whether the reactions are reversible and to measure the equilibrium points, and (2) to study the exact nature of the mechanism of the action of sodium ethylate, and other ethylates, especially in the light of our other work with ethylates, phenolates, etc., which has shown that

[1] Vorländer: Ber. d. chem. Ges., **36**, 268. Karl Elbs: Kohlenstoff-Verbindungen, **1889**, p. 34. Marshall and Acree: This Journal, **49**, 130. Hofmann: Ber. d. chem. Ges., **2**, 120; **3**, 772. Bamberger: *Ibid.*, **15**, 2164. Schiff: *Ibid.*, **9**, 1316. Wurtz: Ann. chim. phys., [3] **42**, 43. Kremann: Monats. Chem., **26**, 783; **29**, 23. Claisen: Ber. d. chem. Ges., **20**, 646. Kossel, Krüger and Obermüller: Z. physiol. Chem., **15**, 321; **16**, 153. Purdie: J. Chem. Soc., **39**, 344; **47**, 863, 867; **59**, 469. Friedländer and Mähly: Ann. Chem. (Liebig), **229**, 210.

[2] Nef: Ann. Chem. (Liebig), **287**, 280. Dains: J. Am. Chem. Soc., **21**, 136. McKee: This Journal, **26**, 209; **36**, 209; **42**, 1.

[3] Dr. Marshall's work was completed in 1911 and Dr. Harrison's in 1912. We had hoped to complete this investigation by studying the action of potassium and lithium ethylates on benzimido ethyl ester and acetimido ethyl ester to learn whether the same value for Ki is obtained for all ethylates, and different values for K_m are found. Since both Dr. Harrison and Dr. Marshall have been compelled to withdraw from the work it seems best for their interests to publish this incomplete study at this time. The final corrections will be made when these studies are completed.

we can express the reaction velocities as functions of the concentrations of both the ethylate ions and the nonionized sodium ethylate.

In another article[1] we have shown that in every case studied the reaction

$$RC \vdots N + C_2H_5OH \rightleftarrows RC(:NH)OC_2H_5$$

does not take place appreciably of itself, but, when catalyzed by ethylates, is reversible. The equilibrium point is the same whether measured from the nitrile or from the imido ester, although slow disturbing side reactions make the agreement in some cases less satisfactory than desired. The equilibrium point varies very widely with the different compounds. The per cent. of imido ester formed is illustrated by the following examples: butyronitrile, 0.90; propionitrile, 1.75; acetonitrile, 2.50; *p*-tolunitrile, 6.8; benzonitrile, 14.0; *p*-chlorobenzonitrile, 25.85; *p*-bromobenzonitrile, 27.2; *m*-bromobenzonitrile, 38.5; *p*-nitrobenzonitrile, 62.0; *m*-nitrobenzonitrile, 78.0; diisoamylcyanoamide, 98.0. The equilibrium point varies rather widely in some cases with changes in the concentrations of the nitrile and the ethylate, but fluctuates very little in other examples. Different ethylates catalyze the reaction with different velocities and the equilibrium points also often vary in such cases. The velocity of the reaction varies greatly with the different nitriles, the *p*-nitrobenzonitrile and chloroacetonitrile reacting very rapidly, whereas *o*-tolunitrile hardly adds alcohol at all.

With this point settled, *we turned our attention to the question whether the sodium ethylate reacts catalytically through the influence of the ethylate ions, or the nonionized sodium ethylate, or both.* This problem and analogous ones are of all the more interest to us because the sodium ethylate acts catalytically in the older sense in that it brings about its chemical changes by its mere presence and is not appreciably changed in its activity, whereas in the reactions with alkyl halides the sodium ethylate is entirely transformed into the end products. It was all the more desirable to us to study

[1] Marshall and Acree: This Journal, **49**, 127.

this and other similar reactions, therefore, to connect these limiting cases in which, on the one hand, the catalyzer is apparently not changed at all, with those in which, on the other hand, it is completely decomposed. It is of the highest importance that we have connected these limiting cases experimentally and shown that fundamentally there is no primary difference in the mechanism of the action of sodium ethylate in the two cases, the *apparent* dissimilarities really depending on a secondary factor, the stability or neutrality of intermediate products, and the tendency of the particular solution to yield the most nearly neutral system. This can be illustrated readily in such equations as the following:

$$\left\{\begin{array}{l} C_2H_5\overline{O} + IC_2H_5 \rightleftarrows C_2H_5\overline{O}.IC_2H_5 \longrightarrow \overline{I} + (C_2H_5)_2O \\ C_2H_5\overline{O} + CH_3C:N \rightleftarrows CH_3C(:\overline{N})OC_2H_5 + C_2H_5OH \longrightarrow \\ \qquad\qquad\qquad\qquad CH_3C(:NH)OC_2H_5 + C_2H_5\overline{O} \end{array}\right.$$

$$\left\{\begin{array}{l} C_2H_5ONa + IC_2H_5 \rightleftarrows C_2H_5ONa.IC_2H_5 \longrightarrow NaI + (C_2H_5)_2O \\ C_2H_5ONa + CH_3C:N \rightleftarrows CH_3C(:NNa)OC_2H_5 + \\ \qquad\qquad C_2H_5OH \longrightarrow CH_3C(:NH)OC_2H_5 + NaOC_2H_5 \end{array}\right.$$

Stieglitz and Schlesinger[1] have studied, in aqueous solutions, the reverse of this reaction, the decomposition of imido esters, in the presence of barium hydroxide as catalytic agent. They followed the ideas of Arrhenius,[2] Ostwald,[3] van't Hoff,[4] Warder,[5] Reicher,[6] Spohr,[7] Hemptinne,[8] Löwenherz,[9] and others, who had shown that ordinary esters are saponified by bases (and acids) with a velocity approximately proportional to the concentration of the hydroxyl[10] (and hydrogen) ions. As

[1] THIS JOURNAL, **39**, 719 (1908).

[2] Z. physik. Chem., **1**, 110 (1887).

[3] J. prakt. Chem., [2] **28**, 449 (1883).

[4] Études de dynamique chimique.

[5] THIS JOURNAL, **3**, 340 (1882).

[6] Ann. Chem. (Liebig), **228**, 257 (1885).

[7] Z. physik. Chem., **2**, 194 (1888).

[8] *Ibid.*, **13**, 561 (1894); **31**, 35 (1899).

[9] *Ibid.*, **15**, 395 (1894).

[10] Miss Marion Brown is now engaged on the analogous study of the saponification of thioesters by sodium, potassium, lithium, ammonium, etc., sulphydrates in absolute ethyl alcohol in order to learn whether both the ionized and nonionized sulphydrates react with the thioesters. The much smaller ionization of these salts in alcohol will allow us to measure the possible activity of the nonionized sulphydrates much better than can be done in aqueous solutions in which the concentration of the nonionized sulphydrate is much smaller than in alcoholic solutions of the same concentration.

a result of their very fine experimental work, they came to the conclusion that an imido ester is decomposed completely into a nitrile and an alcohol *with a velocity proportional to the concentration of the hydroxyl ions and anions of the imido ester.* Stieglitz has admittedly[1] overlooked a principle brought out by one of us, namely, that the *nonionized compounds*, such as barium hydroxide and barium imido ester salts, may be concerned in such reactions. It can be shown that Stieglitz's excellent work harmonizes better with our theory than with his, and that our work, in which we can more accurately measure all the necessary data, leads to the belief that he has perhaps interpreted his experiments unfortunately in that he did not consider the fact that BOTH *the nonionized barium hydroxide and the hydroxyl ions, and nonionized and ionized imido ester salts, may be concerned in the reaction.*

Before our own work was undertaken we examined Stieglitz's data and saw that we secure constants just as good as his if we assume that $K_i = K_m$ for barium hydroxide and that a *gram molecule of nonionized barium hydroxide is just as effective in decomposing imido esters as is a gram ion of hydroxyl ions.* The reasons for the apparent equal validity of these two different interpretations of the experimental work of Stieglitz and Schlesinger is that in the solutions studied the barium hydroxide is so nearly completely ionized, 93 to 97.5 per cent., that the small influence of the nonionized portion, 2.5 to 7 per cent., is masked by the experimental errors necessarily involved in even this fine work. These uncertainties are apparent when we see that the widest variation in K_V in a given series sometimes becomes as high as 23 and 25 per cent., as in Tables XXV*b* and XV*b*, and averages about 9 per cent. for all of the series.

In the following tables we have given the essential details of Tables XX, XXIV, XXVIII, XXXII and XXXVI in Schlesinger's article. In the first column are given the concentrations of barium hydroxide used, in the second the value of K_V, in the third the value K_{OH}, or K_i, obtained by

[1] THIS JOURNAL, **39**, 403. J. Am. Chem. Soc., **34**, 1688, 1689, 1690, 1694.

Schlesinger, in the fourth the deviation of each number in Column 3 from the mean of the entire column, in the fifth the constants calculated simply from the concentration of the barium hydroxide on our assumption that perhaps $K_i = K_m$, and in the sixth the deviation of each number in Column 5 from the mean of the entire column. We did not take the trouble to refer the constants in Column 5 to the same units used by Schlesinger but give simply the quotients of corresponding numbers in Columns 1 and 2. The errors involved in the two methods of calculation, as shown in Columns 4 and 6, are the points of real interest.

Table XX

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
5.90	102	0.887	+3.86	17.28	+5.56
5.80	100	0.885	+3.75	17.24	+5.31
11.40	193	0.873	+2.23	16.93	+4.03
12.00	203	0.871	+1.99	16.91	+3.91
31.80	511	0.837	—1.99	16.07	—1.83
31.10	497	0.833	—2.46	15.98	—2.38
46.60	742	0.840	—1.64	15.92	—2.75
(48.00)	(741)	(0.812)	(—4.92)	(15.44)	(—5.69)
70.20	1090	0.835	—2.23	15.53	—5.13
70.60	1090	0.830	—2.81	15.44	—5.69
		0.854		16.37	

Table XXIV

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
35.90	205	0.298	—0.67	5.71	—0.175
35.70	202	0.298	—0.67	5.66	—1.049
52.20	299	0.301	+0.33	5.73	+0.175
53.50	310	0.290	—3.33	5.79	+1.223
70.10	401	0.307	+2.33	5.72	±0.000
70.40	402	0.307	+2.33	5.71	—0.175
		0.300		5.72	

Table XXVIII

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
30.50	152	0.255	+6.69	4.98	+9.45
30.70	171	(0.285)	....	....	....
61.50	255	0.220	—7.90	4.54	—0.22
64.30	291	0.241	+0.83	4.55	0.00
45.60	207	0.339	0.00	4.15	—8.79
46.20	210	0.239	0.00	4.53	—0.43
		0.239		4.55	

Table XXXII

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
30.90	67.6	0.114	0.00	2.19	+0.92
32.20	67.5	0.109	—4.38	2.10	—3.22
46.20	101	0.115	+0.88	2.19	+1.38
46.50	109	0.123	+7.90	2.34	+7.83
61.50	130	0.113	—0.88	2.11	—2.76
61.60	128	0.111	—2.63	2.08	—4.15
		0.114		2.17	

Table XXXVI.

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
32.70	510	1.62	+0.62	15.6	+1.30
43.70	690	1.66	+3.11	15.8	+2.60
62.50	930	1.55	—3.72	14.9	—3.25
		1.61		15.4	

When these tables are inspected it is seen that the errors in Columns 4 and 6 are uniformly of the same magnitude. Table XX is the least satisfactory one given by Schlesinger, the variations in a given series amounting to 25 per cent. in some cases. If Table XX is omitted, the average of all the values given in Column 4 is 2.14 per cent., while that of Column 6 is identically the same. If Table XX is included, the average of Column 4 is 2.25 per cent. and that of Column 6 is 2.71 per cent. When we recall that the average maximum variation of the constants in a series is 9 per cent., it is seen that

this difference between 2.71 per cent. and 2.25 per cent. is well within the experimental errors. We could be as fully justified, therefore, in believing that barium hydroxide acts through *both* its nonionized form and the hydroxyl ions, as are Stieglitz and Schlesinger in using the theory that the imido esters are decomposed by hydroxyl ions alone in a way shown by Arrhenius, Ostwald, and others to hold for ordinary esters, and our work on the ethylates presented in the following paragraphs leaves no doubt that our point of view is preferable.

For this reason we have chosen alcohol for use as the solvent, whenever possible, for studying reactions; the nonionized salt is present in much larger concentrations and its influence can be measured with much greater accuracy. Our own work in alcoholic solutions has shown that the velocity of decomposition of imido esters is a function of the concentrations of *both* the ethylate ions and the sodium ethylate molecules, the values $K_i : K_m = 0.1172 : 0.0976$ and $K_i : K_m = 0.344 : 0.228$ having been found for benzimido ethyl ester and acetimido ethyl ester, for example. We consider that, in this case, as in others, sodium, potassium and other ethylates are *bases* in ethyl alcohol analogous to the corresponding hydroxides in water. If we were to work with sodium ethylate solutions more dilute than 0.002 N, the per cent. of ionization of the ethylate would be found to be above 90 per cent., and, as in Stieglitz's work with barium hydroxide, the reaction velocities would be so nearly proportional to the concentration of the ethylate ions that the activity of the sodium ethylate molecules would be masked by experimental errors to just the same extent observed in the work of Stieglitz and Schlesinger with barium hydroxide. Fortunately we can work with solutions as concentrated as 0.25 N, in which the relative concentration of the ethylate ions is only about 30 per cent. and that of the nonionized sodium ethylate 70 per cent., and in which the change due to the molecules is about 20 times as large as in 0.002 N solutions and hence easily measured. Our work shows the interpretation of Stieglitz to be *partially* correct in that it proves that imido esters are decomposed by

hydroxyl (and ethylate) ions, and further substantiates the still broader theory that both ions and nonionized compounds must be considered in the study of all reaction mechanisms.

If the rate of reaction of the imido ester, or of the nitrile, is practically zero in the *absence* of ethylates, and in their *presence* it is a function of the concentrations of both the ethylate ions and the nonionized sodium ethylate, the reaction velocity must be expressed by the equation,

$$\frac{dx}{dt} = K_i\,[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate} \times (A_1 - x)$$
$$- K_2\,[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate} \times (A_2 + x)$$

in which it is assumed that the concentration of the alcohol is practically a constant, involved in K_2, that α is the per cent. of ionization of the sodium ethylate, $C_{ethylate}$, that K'_i is the catalytic effect of the ethylate ions, that K'_m is the catalytic effect of the nonionized sodium ethylate, that A_1 is the original concentration of the imido ester, that A_2 is the original concentration of the nitrile, and that x is the change in concentration of the imido ester in the time t. The integral of this equation is

$$K_V = \frac{1}{t}\ln\frac{KA_1 - A_2}{KA_1 - A_2 - (K+1)x} = \frac{(K_1 + K_2)[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate}}{[K_i\alpha + K_m(1-\alpha)] \times C_{ethylate}}$$

in which

$$K = \frac{K_1[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate}}{K_2[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate}} = \frac{K_1}{K_2}, \text{ and}$$
$$K_i = K'_i\,(K_1 + K_2), \text{ and } K_m = K'_m(K_1 + K_2).$$

It is to be noted that in developing these equations we have assumed the ratios $K_i : K_m$, for the reverse reactions, to be constant, an assumption which leads to the conclusion that K must be constant. We actually find K to be constant within the experimental errors, and hence independent of the concentration of the sodium ethylate. We have developed similar equations to apply to those cases in which K varies. K_V should be constant with varying concentrations of nitrile and a constant concentration of sodium ethylate, provided

that no double compounds are formed, and the nitrile does not visibly alter the physical properties of the solutions. As a matter of experiment we find in Table XIX an increase of only 7.4 per cent. in K_V with an increase of 800 per cent. in the concentration of acetonitrile. We have therefore used only one concentration of nitrile, 0.250 N, in all of the quantitative studies. In the remainder of the article we shall use the expressions K_i and K_m instead of $K'_i\ (K_1 + K_2)$ and $K'_m\ (K_1 + K_2)$ merely for convenience. Having then obtained the different values K_V, K'_V, K''_V, for the different concentrations of sodium ethylate, $1/V$, $1/V'$, $1/V''$, etc., we need only multiply the different values of K_V by the values for the corresponding V and we obtain a series of simultaneous equations:

$$K_n = K_i\alpha + K_m(1 - \alpha),$$
$$K'_n = K_i\alpha' + K_m(1 - \alpha'),$$
$$K''_n = K_i\alpha'' + K_m(1 - \alpha''), \text{ etc.,}$$

in which K_n, K'_n, K''_n, etc., given in Table XIX, represent the reaction velocities which would be found if the solution were *normal* with respect to sodium ethylate having the degree of ionization α, α', α'', etc. When these equations are solved we obtain in Table XX the values 0.344 and 0.228 for K_i and K_m for acetimido ethyl ester, which are constant within the experimental errors, the ratio $K_i : K_m$ being approximately 1.5. In Table X in the work on benzimido ethyl ester we find the values 0.1172 and 0.0976 for K_i and K_m. This is entirely in harmony with our work on the action of alkyl halides on sodium ethylate, on sodium phenolate and sodium 1-phenyl-3-thiourazole, in which we have found that we can express the reaction velocities as functions of the concentrations of the ions and of the nonionized salts. The ratios $K_i : K_m$ are 2.13, 2.81 and 2.41 for the reaction of sodium ethylate with methyl iodide, ethyl iodide and ethyl bromide, respectively. We have furthermore substituted the values 0.344 and 0.228 in the various equations, $K_n = K_i\alpha + K_m\ (1-\alpha)$, $K'_n = K_i\alpha' + K_m\ (1-\alpha')$, etc., corresponding to the different values of α, α', α'', etc., and have obtained values for "K_n calculated" which are shown in Table XXI to agree very closely

with the "K_n found" obtained experimentally. We may conclude then that, in some respects, sodium ethylate behaves toward the unsaturated nitriles, $CH_3C \vdots N$, just as it does towards the unsaturated alkyl halides, $CH_3I \equiv$, an unstable addition product probably being formed as an intermediary step in both cases on account of the unsaturated character of all these substances.

But we have fortunately been able to go one step further in this work. When we examine the above equations we see that we could look upon the reactions as an *acceleration* of the purely *ionic* reaction by another reaction which we have called the nonionic reaction, whose coefficient is K_m. This *salt effect* is a very important phase of reaction mechanisms, is not very well understood at present, and has been a subject of investigation by us in all of our quantitative studies with the urazoles, amides, ethylates, etc., etc., and it has furthermore received attention from a large number of other workers. Arrhenius[1] suggested that this salt effect is due to the ions of the salt, and Euler[2] believed that these ions change the ionization of water and hence influence the rate of those reactions in which water is one of the reacting constituents. Stieglitz has adopted these ideas and applied them to his fine imido ester work.[3] He thinks that he has found evidence for the support of their theories, especially the idea of Euler, and believes that the "salt effect" of the cation is chiefly only a change in the active mass, or per cent. of ionization, of the water. But we have shown in another article[4] that Stieglitz has perhaps made an unfortunate interpretation of his own experimental work. His experimental data have been recalculated by us and found to give a full and complete verification of our ideas of "salt catalysis" rather than of those of Arrhenius and Euler, and prove that the "salt effect" is chiefly the transformation of the nonionized imido ester salt, augmented by an "abnormal salt catalysis."

[1] Z. physik. Chem., **1**, 110 (1887).
[2] *Ibid.*, **32**, 357 (1900).
[3] This Journal, **39**, 437 (1908); **39**, 586; **39**, 719. J. Am. Chem. Soc., **32**, 222 (1910).
[4] This Journal, **48**, 369; **49**, 120.

$$C_6H_5C(:\overset{+}{N}H_2)OC_2H_5 + H_2O \longrightarrow$$
$$C_6H_5C(OH)(\overset{+}{N}H_3)OC_2H_5 \longrightarrow C_6H_5COOC_2H_5 + \overset{+}{N}H_4$$
$$C_6H_5C(:NH_2Cl)OC_2H_5 + H_2O \longrightarrow$$
$$C_6H_5C(OH)(NH_3Cl)OC_2H_5 \longrightarrow C_6H_5COOC_2H_5 + NH_4Cl$$

Starting from the idea that the "salt effect" may be due to another reaction involving nonionized complex compounds, perhaps in traces in some cases, we have developed the above equation, $K_n = K_i\alpha + K_m(1 - \alpha)$, to express such a reaction when the nonionized salt (*e. g.*, sodium ethylate) forms the nonionized complex, and also the alternate equation, $K_n = K_i\alpha + K_m(\alpha^2/V)$ which applies if the *nonionized* complex compound is formed from the *anion and cation* together. We have shown in another paper[1] that the first equation applies in all cases whereas the second applies in only two cases, which may be due to *algebraical accidents*. It will now be shown that the first equation applies very closely in the present work, whereas the second equation leads to no constants at all.

Let us take the case of a solution of 0.25 N acetimido ethyl ester and 0.0625 N sodium ethylate for which we used the equation $K_n = K_i\alpha + K_m(1 - \alpha)$, and the found values $K_n = 0.2848$, $\alpha = 0.481$, $K_i = 0.344$ and $K_m = 0.228$. If the equation $K_n = K_i\alpha + K_m(\alpha^2/V)$ were true, then the addition of sodium iodide to this solution of sodium ethylate and imido ester should suppress the ionization of the sodium ethylate in accordance with the isohydric principle, which we have proven experimentally, and should therefore decrease the value of $K_i\alpha$. But the *decrease* in α, the concentration of the ethylate ion, is small in comparison with the *increase* in α/V, the concentration of the sodium cations. If, for instance, we were to add 7 equivalents of sodium iodide to 0.0625 N sodium ethylate and 0.25 N acetimido ethyl ester, the ionization of the sodium ethylate should change from that of a N/16 solution, 0.481, to that of a N/2 solution, 0.234, in accordance with the isohydric principle, and the value of $K_i\alpha$ would change from $0.344 \times 0.481 = 0.1655$ to $0.344 \times 0.234 = 0.0805$, a decrease of 51 per cent. But if we use

[1] THIS JOURNAL, **48**, 376.

the calculated value, about 8, for K_m, the value of $K_m(\alpha^2/V)$ would change from 0.118 to $8 \times 0.234 \times 0.169 = 0.3164$, an increase of about 168 per cent. As a consequence, then, the value of K_n should *increase* from 0.2848 found to 0.3969, or 39 per cent., when 7 equivalents of sodium iodide are added. If the total change were one of the cations and anions together in one reaction, increased by the cations in another reaction, the rate, K_v, would change from 0.0178, found, for the 0.0625 N sodium ethylate alone, to about 0.0778, an increase of 337 per cent. by the 7 equivalents of sodium iodide. If the reaction were one of sodium ethylate molecules, increased by another reaction of the cations, the velocity would change from 0.0178 found for the 0.0625 N sodium ethylate alone, to 0.0690 in the presence of 7 equivalents of sodium iodide, *an increase of 288 per cent.* As a matter of fact it *decreases* to 0.2512, and no one of these three hypotheses holds in our work. We have also tried, without success, to apply the formulas $K_n = K_i\alpha + K_m$, $K_n = K_i + K_m(1 - \alpha)$, to a number of cases. When we finally collect our experimental material we shall again consider all of these hypotheses.

But let us calculate what should be the change if our alternate theory holds, and the equation $K_n = K_i\alpha + K_m(1 - \alpha)$ represents the true course of all the reactions studied, even when an *added* salt changes the reaction velocity through the so-called "salt catalysis." As stated above, the value of $K_i\alpha$ should be changed from $0.344 \times 0.481 = 0.1655$ to $0.344 \times 0.234 = 0.0805$, and the value $K_m(1 - \alpha)$ should consequently be changed from $0.288 \times 0.519 = 0.118$ to $0.228 \times 0.766 = 0.1745$. K_n consequently should be changed from $0.344 \times 0.481 + 0.228 \times 0.519 = 0.2838$ to $0.344 \times 0.234 + 0.228 \times 0.766 = 0.2551$. We find actually experimentally 0.2512 which differs from this calculated value only 1.6 per cent. but differs by 58 per cent. from the 0.3969 calculated on the first of the three above assumptions. The same close agreement with our theory is found when varying mixtures of sodium ethylate and sodium iodide, and sodium ethylate and sodium bromide, are used, and we can therefore conclude *that in this case* the mysterious so-called

"salt catalysis" is nothing more than a change, produced by the added salt, in the concentrations of the reacting constituents, as demanded by the Arrhenius-Barmwater theory of isohydric solutions.[1]

It is clear then that we have secured some experimental evidence concerning the nature of the catalytic action of added salts in this case and four others and that we can explain the *chief part* of this salt catalysis *in all cases yet studied by us* on the *rational basis* of the transformation of a nonionized complex compound formed by the reaction of, for example, the imido ester and the nonionized catalyzer, or on the basis of the reaction of the *nonionized catalyzer* with the imido ester *directly*, without the assumption of the formation of a complex compound. In the case of sodium ethylate, sodium phenolate, sodium thiourazole, and imido ester salts, the nonionized salt is present in large amounts and disappears in the reaction with the alkyl halide or water, the addition products,

$$C_2H_5I.C_2H_5ONa,\ C_2H_5C(OH)(NH_3Cl)(OC_2H_5),\ \text{etc.},$$

perhaps, forming the intermediate steps. In the case of the *pure* catalysis of the imido ester, or nitrile and alcohol, by sodium ethylate the nonionized salt does not disappear in the reaction, and yet the "salt effect" is due *solely* to the increase in the concentration of the *nonionized* sodium ethylate, which is also approximately true in the above cases in which the nonionized compound disappears as a result of the reaction: there is, however, a small "abnormal salt effect" in these latter cases. In some other reactions as pointed out before, it may be found that the "salt catalysis" is produced on account of the formation of complex compounds, in *traces* in some cases, from certain constituents and *anions and cations together*, while in still other cases the salt catalysis may be due to the formation of other anions or cations, or nonionized complex salts, having reaction velocities greater or smaller than those of the original constituents. The formulas

$$C_6H_5C(:NH_2Cl)(OC_2H_5).KCl,\ C_6H_5C(:NH_2Cl)(OC_2H_5).\overset{+}{H},$$

$$C_2H_5ONa.C_2H_5I.NaI \text{ and } C_2H_5ONa.IC_2H_5.\overset{+}{Na}$$

[1] Z. physik. Chem., **28**, 424 (1899). *Ibid.*, **45**, 557 (1903).

are illustrations of the idea. The variations of this central idea are manifold. The question then whether the *added salt* will *increase* or *decrease* the reaction velocity will naturally depend simply upon the relative magnitudes of K_i and K_m, or other constants involved. If, for instance, K_m is the larger, the addition of the *added or catalyzing salt increases* the reaction velocity because the increase in the concentration of the nonionized form of the reactive salt causes the increase in $K_m(1 - \alpha)$ to be larger than the attendant decrease in $K_i\alpha$. The added salt suppresses the ionization of the active salt, and *lowers* the reaction velocity when K_i is larger than K_m because the decrease in $K_i\alpha$ is then greater than the increase in $K_m(1 - \alpha)$. This last case corresponds to all the problems that we have yet studied and to our interpretation of Stieglitz's imido ester work. If $K_m = K_i$ the added salt cannot change the reaction velocity, unless for reasons other than the ones discussed here. There may be "abnormal salt effects" in many cases, some of which we are studying.

This idea of salt catalysis is far more fortunate than the *assumption* by Euler and Stieglitz that the added salt changes the active mass, or per cent. of ionization, of the water or alcohol to a considerable extent. All the evidence is against any such idea that the water can change more than a very few per cent. in ionization, and their theory is clearly wrong for the reasons pointed out in earlier articles.[1]

EXPERIMENTAL

Acetonitrile and Acetimido Ethyl Ester

The bath used in this investigation has already been described.[2] Its temperature was constant at 25° to within ±0°.005. The alcohol used was dehydrated by boiling it with lime. No alcohol was used which contained more then 0.06 per cent. water, and in general the amount of water was considerably less than this. The *acetimido ethyl ester hydrochloride* was prepared as already described in another article.[3] The solutions of sodium ethylate were prepared by dissolving

[1] See especially This Journal, **41**, 475; **48**, 369.
[2] H. C. Robertson, Jr.: Diss., Johns Hopkins Univ., **1910**.
[3] Marshall and Acree: This Journal, **49**, 146.

pure sodium in cold alcohol. The measurements of the velocity of the reaction were carried out as follows: A solution of the required strength of acetimido ethyl ester hydrochloride was made by weighing the substance, transferring it to a graduated flask, dissolving it in alcohol as quickly as possible, and diluting the solution to the mark at 25°. A solution of sodium ethylate was prepared having the required strength plus the amount necessary to liberate the free imido ester from its hydrochloride. Thus, if 0.25 N imido ester and 0.25 N sodium ethylate were required, equal volumes of a 0.5 N solution of imido ester hydrochloride and N solution of sodium ethylate were mixed. The time of mixing the two solutions was noted, and aliquot portions (10 or 20 cc.) were pipetted out at various intervals and titrated with standard hydrochloric acid. The equilibrium point was determined by two duplicate titrations after the solution had stood overnight or longer. The equilibrium point from the imido ester side did not correspond to that obtained by starting with the nitrile. This is due to three causes: (1) to a small amount of ammonium chloride present in the original imido ester hydrochloride, (2) to the decomposition of the solution of the imido ester hydrochloride into ortho-ester and ammonium chloride during the short time necessary for bringing it to 25° and diluting the solution, and (3) to the decomposition of the imido ester hydrochloride into acetamide and ethyl chloride during this short time. The ammonia thus formed when the sodium ethylate solution is added remains practically constant throughout the reaction. The concentration of the ethylate is not influenced by this, and as the values for x with varying t are obtained from the difference in the alkalinity of the solution, x is therefore not affected. The only error to be taken into consideration is the value of A, or the concentration of the imido ester. This can be corrected for by considering the equilibrium point obtained by starting with the nitrile as the true one. For instance, we see in Table I that with 0.25 N acetonitrile and 0.5 N, 0.25 N, 0.125 N, and 0.0625 N sodium ethylate an average of 1.73 per cent. imido ester is formed at equilibrium. If our value of A_1 is 12.50, we have

$12.50 \times 0.0173 = 0.21$ as the amount of imido ester which should be present in the solution at equilibrium. This would give us as the equilibrium value of x $12.50 - 0.21 = 12.29$, but the value found for x is 12.13. We have, therefore, a correction for the ammonia formed amounting to 0.16. This gives us as a correct value for A, $12.50 - 0.16 = 12.34$. The amount of ammonia varies somewhat, as would be expected, in the individual experiments, but on an average amounts to a little over one per cent. The correction for the change in concentration of the imido ester has been applied in all cases.

We first proved that the free imido ester does not decompose with any appreciable velocity unless catalyzed by the ethylate. A solution of the imido ester hydrochloride was treated with nine-tenths of the theoretical amount of ethylate and titrated from time to time by Dr. C. N. Myers.

Time	3.5 hrs.	4 hrs.	23 hrs.	29 hrs.	46 hrs.	9 days
Cc. 0.2 N HCl	9.77	9.70	9.71	9.70	9.71	9.31

The amount of change due to the *uncatalyzed*, or spontaneous decomposition of the free imido ester cannot produce any appreciable error in our constants. When portions of this solution were treated with N/8 sodium ethylate the imido ester was decomposed as usual.

Since the mass of the alcohol can be considered practically constant, we have a reversible monomolecular reaction expressed by the following equations:

$$\frac{dx}{dt} = K_1(A_1 - x) - K_2(A_2 + x)$$

in which A_1 is the original concentration of the imido ester, A_2 that of the nitrile, and x the concentration of the nitrile formed during the reaction. At equilibrium, we have

$$K = \frac{K_1}{K_2} = \frac{A_2 + x}{A_1 - x}$$

Substituting K for K_1/K_2 we get

$$\frac{1}{t} \ln \frac{KA_1 - A_2}{KA_1 - A_2 - (K+1)x} K_1 + K_2 = K_V.$$

Since $A_2 = 0$ in all our experiments, we can simplify the above expression and obtain

$$\frac{1}{t} \ln \frac{KA_1}{KA_1 - (K + 1)x} = K_1 + K_2 = K_V$$

in which

$$K = \frac{x}{A_1 - x}$$

K_n is obtained by dividing K_V by the concentration, $1/V$, of the sodium ethylate. All concentrations in this work are those obtained *after mixing* the solutions. The two following tables on acetonitrile and sodium ethylate are taken from a previous article[1] by the authors.

Table I—0.25 N Acetonitrile[2] and Sodium Ethylate

Conc. sodium ethylate	Per cent. imido-ester formed
0.5 N	1.68
0.25 N	1.80
0.125 N	1.64
0.0625 N	1.80
0.03125 N	1.60
0.015625 N	1.60
Average used	= 1.73

Table II—Acetonitrile and Sodium Ethylate

Conc. aceto-nitrile	Conc. sodium ethylate	Per cent. imido-ester formed
0.5 N	0.5 N	1.44
0.25 N	0.25 N	1.80
0.125 N	0.25 N	2.48
0.0625 N	0.25 N	2.56

Table III—Ionization of Sodium Ethylate in Absolute Alcohol at 25°

V	α	$(1 - \alpha)$
1	0.148	0.852
2	0.234	0.766
4	0.312	0.688
8	0.393	0.607
16	0.481	0.519
32	0.577	0.423
64	0.686	0.314

[1] Marshall and Acree: This Journal, 49, 149.

[2] The last two values were worked out by Dr. C. N. Myers.

Table IV[1]—0.25 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate

$A_1 = 12.34$ $A_2 = 0$ $K = 55.1\ (57.8)$[2]

t	x	K_V
25	10.11	0.0689
31	10.71	0.0693
37	11.18	0.0689
46	11.61	0.0684
	12.13	

Average = 0.0689
K_n = 0.2756

Table V—0.25 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate

$A_1 = 12.05$ $A_2 = 0$ $K = 54.0\ (56.4)$

t	x	K_V
21	9.06	0.0691
28	10.15	0.0695
34	10.66	0.0680
40	11.04	0.0675
	11.84	

Average = 0.0685
K_n = 0.2740

Table VI—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.22$ $A_2 = 0$ $K = 60.0\ (57.2)$

t	x	K_V
5	1.98	0.0359
15	4.79	0.0339
27	7.10	0.0332
40	9.41	0.0382
91	11.41	0.0332
	12.01	

Average = 0.0341
K_n = 0.2728

[1] The values in Tables IV and V are not used in the final calculations because in these concentrations the abnormal physical properties become noticeable. Dr. Meyers has obtained similar results in his work on the addition of ethyl alcohol to *p*-bromobenzonitrile in the presence of sodium, potassium and lithium ethylates.

[2] The values of K given outside the parentheses in each of the following tables are those calculated from the data for the corresponding concentrations in Table I, the values inside the parentheses being derived from the *average used*, 1.73. The influence of K in the formula is so small that identically the same reaction velocity is obtained by the use of either value of K.

Table VII—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.30$	$A_2 = 0$	$K = 60.4\ (57.6)$
t	x	K_V
5	2.07	0.0375
15	5.03	0.0359
25	6.91	0.0339
40	8.96	0.0339
60	10.52	0.0341
90	11.53	0.0341
	12.09	
	Average =	0.0349
	K_n =	0.2792

Table VIII—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.23$	$A_2 = 0$	$K = 60.1\ (57.2)$
t	x	K_V
10	3.52	0.0345
17	5.20	0.0334
23	6.44	0.0334
31	7.70	0.0330
45	9.35	0.0334
60	10.46	0.0341
90	11.42	0.0336
	12.02	
	Average =	0.0336
	K_n =	0.2688

Table IX—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.23$	$A_2 = 0$	$K = 54.7\ (57.2)$
t	x	K_V
15	2.90	0.0184
25	4.33	0.0179
35	5.51	0.0175
50	7.01	0.0175
66	8.23	0.0174
126	10.73	0.0177
147	11.10	0.0174
	12.02	
	Average =	0.0177
	K_n =	0.2832

Table X—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.27$ $A_2 = 0$ $K = 54.8\ (57.4)$

t	x	K_V
25	4.39	0.0181
35	5.63	0.0180
45	6.66	0.0179
60	7.93	0.0179
80	9.15	0.0178
115	10.53	0.0179
∞	12.06	

Average = 0.0179
K_n = 0.2864

Table XI—0.25 N Acetimido Ethyl Ester and 0.03125 N Sodium Ethylate

$A_1 = 12.15$ $A_2 = 0$ $K = 59.7\ (56.9)$

t	x	K_V
15	1.53	0.00914
30	2.91	0.00928
45	4.04	0.00917
65	5.40	0.00924
90	6.74	0.00898
110	7.65	0.00930
156	9.13	0.00928
262	10.92	0.00937
∞	11.94	

Average = 0.00921
K_n = 0.2947

Table XII—0.25 N Acetimido Ethyl Ester and 0.03125 N Sodium Ethylate

$A_1 = 11.92$ $A_2 = 0$ $K = 58.5\ (55.8)$

t	x	K_V
25	2.44	0.00933
41	3.71	0.00928
56	4.72	0.00921
71	5.63	0.00924
92	6.68	0.00919
122	7.79	0.00898
∞	11.71	

Average = 0.00919
K_n = 0.2941

Table XIII—0.25 N Acetimido Ethyl Ester and 0.015625 N Sodium Ethylate

$A_1 = 24.44$	$A_2 = 0$	$K = 60.2\ (57.2)$
t	x	K_V
15	1.60	0.00477
30	3.11	0.00477
50	4.91	0.00479
80	7.50	0.00484
104	9.17	0.00479
210	15.03	0.00491
333	18.92	0.00500
∞	24.02	

Average = 0.00484
K_n = 0.3098

Table XIV—0.25 N Acetimido Ethyl Ester and 0.015625 N Sodium Ethylate

$A_1 = 24.36$	$A_2 = 0$	$K = 59.8\ (57.0)$
t	x	K_V
15	1.70	0.00489
30	3.30	0.00491
51	5.21	0.00481
90	8.29	0.00472
207	14.92	0.00474
292	17.82	0.00470
∞	23.94	

Average = 0.00479
K_n = 0.3066

Table XV—0.5 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 24.27$	$A_2 = 0$	$K = 66.4$
t	x	K_V
11	8.35	0.0382
17	11.87	0.0394
26	15.49	0.0389
33	16.70	0.0352
40	18.24	0.0348
60	21.12	0.0341
85	22.80	0.0329
∞	23.91	

Average = 0.0362
K_n = 0.2896

Table XVI—0.5 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 24.07$	$A_2 = 0$	$K = 66.0$
t	x	K_V
25	14.99	0.0401
32	16.59	0.0375
41	18.54	0.0371
53	20.37	0.0368
67	21.70	0.0368
∞	23.70	
	Average =	0.0375
	K_n =	0.3000

Table XVII—0.125 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate

$A_1 = 6.07$	$A_2 = 0$	$K = 39.5$
t	x	K_V
8	2.59	0.0719
16	4.00	0.0705
21	4.50	0.0679
27	4.99	0.0684
33	5.31	0.0689
41	5.54	0.0670
54	5.80	0.0721
∞	5.92	
	Average =	0.0685
	K_n =	0.2740

Table XVIII—0.0625 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate

$A_1 = 6.09$	$A_2 = 0$	$K = 37.1$
t	x	K_V
15	3.71	0.0661
21	4.43	0.0654
26	4.86	0.0658
32	5.22	0.0663
38	5.44	0.0654
45	5.67	0.0690
50	5.73	0.0672
∞	5.93	
	Average =	0.0661
	K_n =	0.2644

The concentrations in the above tables are all expressed after mixing. Referring the reaction velocities for the different dilutions to normal concentration, we obtain comparable values, which we shall designate K_n. The following table gives a résumé of all the above work and was used in calculating the values of K_i and K_m given in Table *XX*.

Table XIX—0.25 N Acetimido Ethyl Ester and Sodium Ethylate

Concentration of sodium ethylate	$K_1 + K_2 = K_V$		K_n
0.125 N	0.0341	0.0342	0.2736
	0.0349		
	0.0336		
0.0625 N	0.0177	0.0178	0.2848
	0.0179		
0.03125 N	0.00931	0.00920	0.2944
	0.00919		
0.015625 N	0.00484	0.00482	0.3084
	0.00479		

Acetimido Ethyl Ester and Sodium Ethylate

Concentration of imido ester	Concentration of sodium ethylate	$K_1 + K_2 = K_V$		K_n
0.5 N	0.125 N	0.0362	0.0369	0.2952
		0.0375		
0.5 N	0.25 N	....		0.2852[1]
0.25 N	0.25 N	0.0692		0.2768
0.125 N	0.25 N	0.0685		0.2740
0.0625 N	0.25 N	0.0661		0.2644

If, in this case of catalysis, we have both the ethylate ion and sodium ethylate molecules concerned in the reaction, we should be able to calculate the constant for the velocity of the ionic and molecular reactions separately, as has been done in the case of the reaction between ethylates and alkyl halides.[2] We have used the equation $K_n = K_i\alpha + K_m(1 - \alpha)$ in which K_i is the ionic velocity and K_m the molecular velocity, and calculated the following values for K_i and K_m, which are seen to be very constant.

[1] Recalculated from the data for 0.5 N imido ester and 0.125 N sodium ethylate.

[2] See other work by Robertson, Marshall, Harrison, Chandler, Myers, Shrader, Brown, Nirdlinger and Rogers: This Journal, **48**, 352; **49**, 116, 127.

Table XX

V	K_i	K_m
8 : 16	0.336	0.238
8 : 32	0.342	0.230
8 : 64	0.346	0.228
16 : 32	0.346	0.228
16 : 64	0.346	0.222
32 : 64	0.348	0.222
Average,	= 0.344	0.228

We have used the values $K_i = 0.344$ and $K_m = 0.228$ in recalculating the values of K_n corresponding to the different concentrations of sodium ethylate used, and have compared these values of "K_n calculated" with those of "K_n found." The agreement is quite satisfactory as can be seen from the following table:

Table XXI—0.25 N Acetimido Ethyl Ester and Sodium Ethylate

Concentration of sodium ethylate	K_n found	K_n calculated	Error in per cent.
0.125	0.2736	0.2736	±0.00
0.0625	0.2848	0.2838	+0.35
0.03125	0.2944	0.2949	—0.10
0.015625	0.3084	0.3076	+0.26
		Average error =	—0.05

A STUDY OF SALT CATALYSIS

After thus learning the effect of the *ethylate ion* and of the *nonionized sodium ethylate* on this reaction, we thought it wise to test this theory further by suppressing the ionization of the sodium ethylate by the addition of sodium iodide in order to see if the new reaction velocities correspond to the new ionization values. This should be the case if the added sodium iodide produces no "abnormal salt effect," the theory of which was discussed fully on page 379. The following tables show, in the main, that the change in the reaction velocity is very close to that calculated from our theory, and that the sodium iodide produces no appreciable "abnormal salt effect." The value of K used was determined experimentally in each case

by measuring the equilibrium point in the corresponding mixture of sodium iodide, sodium ethylate and acetonitrile.

Table XXII—0.25 N Acetimido Ethyl Ester, 0.25 N Sodium Ethylate and 0.25 N Sodium Iodide

$A_1 = 12.45$	$A_2 = 0$	$K = 124$
t	x	K_V
20	9.00	0.0656
26	10.08	0.0651
31	10.70	0.0650
37	11.22	0.0647
44	11.66	0.0654
	12.35	

Average = 0.0651
Calculated = 0.0638
K_V without sodium iodide = 0.0692

0.25 N Acetonitrile and 0.25 N Sodium Ethylate with 0.25 N Sodium Iodide.—Twenty cc. were taken for titration, and required 25.22, 25.24, 25.23 cc. 0.2 N hydrochloric acid. This corresponds to 0.84 per cent. imido ester present at equilibrium.

Table XXIII—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate with 0.125 N Sodium Iodide

$A_1 = 12.03$	$A_2 = 0$	$K = 119$
t	x	K_V
32	7.78	0.0329
45	9.13	0.0322
53	9.71	0.0318
61	10.23	0.0320
68	10.61	0.0322
76	10.91	0.0324
	11.93	

Average = 0.0322
Calculated = 0.0321
K_V without sodium iodide = 0.0342

0.25 N Acetonitrile and 0.1245 N Sodium Ethylate with 0.125 N Sodium Iodide.—Twenty cc. were used for titration, and required 12.73, 12.76 cc. 0.2 N hydrochloric acid. This

corresponds to 0.84 per cent. imido ester present at equilibrium.

Table XXIV—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate with 0.375 N Sodium Iodide

$A_1 = 12.25$	$A_2 = 0$	$K_V = 122$
t	x	K_V
21	5.97	0.0322
25.5	6.77	0.0320
30	7.41	0.0313
41	8.66	0.0304
48	9.37	0.0306
59	10.12	0.0304
69	10.61	0.0300
∞	12.15	

Average = 0.0310
Calculated = 0.0319
K_V without sodium iodide = 0.0342

0.25 N Acetonitrile and 0.1246 N Sodium Ethylate with 0.375 N Sodium Iodide.—Ten cc. were used for titration and required 6.34, 6.33 cc. 0.2 N hydrochloric acid. This corresponds to 0.84 per cent. imido ester present at equilibrium.

Table XXV—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate with 0.0625 N Sodium Iodide

$A_1 = 12.14$	$A_2 = 0$	$K = 120$
t	x	K_V
16	2.98	0.0178
21	3.68	0.0174
27	4.38	0.0167
36	5.42	0.0166
51	6.86	0.0167
67	8.04	0.0164
108	9.99	0.0164
∞	12.04	

Average = 0.0169
Calculated = 0.0171
K_V without sodium iodide = 0.0178

0.25 N Acetonitrile and 0.616 N Sodium Ethylate with 0.0625 N Sodium Iodide.—Ten cc. were used for titration and re-

quired 3.22, 3.19, 3.20 cc. 0.2 N hydrochloric acid. This corresponds to 0.96 per cent. imido ester present at equilibrium.

Table XXVI—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate with 0.1875 N Sodium Iodide

$A_1 = 12.20$	$A_2 = 0$	$K = 121$
t	x	K_V
16	2.81	0.0165
21	3.46	0.0160
34	4.94	0.0155
43	5.98	0.0162
61	7.43	0.0156
84	8.85	0.0156
126	10.41	0.0156
∞	12.10	

Average = 0.0159
Calculated = 0.0165
K_V without sodium iodide = 0.0178

0.25 N Acetonitrile and 0.0626 N Sodium Ethylate with 0.1875 N Sodium Iodide.—Ten cc. were used for titration and required 3.24, 3.26 cc. 0.2 N hydrochloric acid. This corresponds to 0.96 per cent. imido ester present at equilibrium.

Table XXVII—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate with 0.4375 N Sodium Iodide

$A_1 = 12.10$	$A_2 = 0$	$K = 120$
t	x	K_V
20	3.33	0.0162
27	4.26	0.0162
34	5.03	0.0160
42	5.79	0.0157
50	6.48	0.0155
69	7.79	0.0152
81	8.52	0.0153
∞	12.00	

Average = 0.0157
Calculated = 0.0160
K_V without sodium iodide = 0.0178

0.25 N Acetonitrile and 0.0634 N Sodium Ethylate with 0.4375 N Sodium Iodide.—Twenty cc. were used for titra-

tion and required 6.44, 6.43 cc. 0.2 N hydrochloric acid. This corresponds to 0.74 per cent. imido ester at equilibrium.

In the following table we give a résumé of all the above work on the *salt catalysis* produced by sodium iodide.

Table XXVIII—0.25 N Acetimido Ethyl Ester, Sodium Ethylate and Sodium Iodide

Concentration of sodium ethylate	Concentration of sodium iodide	K_V found	K_V calculated	Error in per cent.
0.250 N	0.250 N	0.0651	0.0638	+2.0
0.125 N	0.125 N	0.0322	0.0321	+0.3
0.125 N	0.375 N	0.0310	0.0319	—3.0
0.0625 N	0.0625 N	0.0169	0.0171	—1.2
0.0625 N	0.1875 N	0.0159	0.0165	—3.8
0.0625 N	0.4375 N	0.0157	0.0160	—1.9

Average error = —1.26

The experiments show very clearly that the "salt effect" produced by the added sodium iodide can be interpreted as due *chiefly* to the change in ionization of the sodium ethylate by the sodium iodide and the resulting change in reaction velocity.

Since the acetimido ethyl ester decomposes so nearly completely into acetonitrile and alcohol in the presence of sodium ethylate, we made some calculations to see whether good constants can be obtained by considering the reaction as monomolecular and considering A to be the total change in the concentration of the imido ester. The following corrected tables show that the constants have practically the same value whether calculated in this way or on the correct basis:

Table XXIX—(See Table VIII)

$A = 12.03$

t	$A-x$	AK
10	8.51	0.0345
17	6.83	0.0333
23	5.59	0.0333
31	4.33	0.0329
45	2.68	0.0332
60	1.57	0.0339

Average = 0.0335

$K_1 + K_2 = 0.0336$

Table XXX—(See Table XVII)

$A = 5.92$

t	$A - x$	AK
8	3.33	0.0633
16	1.92	0.0707
21	1.42	0.0691
27	0.93	0.0690
33	0.61	0.0690
41	0.38	0.0670
54	0.12	0.0721

Average = 0.0686
$K_1 + K_2$ = 0.0685

Table XXXI—(See Table XVIII)

$A = 5.93$

t	$A - x$	AK
15	2.22	0.0654
21	1.50	0.0654
26	1.07	0.0659
32	0.71	0.0663
38	0.49	0.0656
50	0.20	0.0677

Average = 0.0660
$K_1 + K_2$ = 0.0661

Benzonitrile and Benzimido Ethyl Ester

Benzimido ethyl ester hydrochloride was prepared by the method described by Pinner[1] with modifications.[2] A mixture of one mole of benzonitrile and 1.25 moles of alcohol (containing not more than 0.06 per cent. water) was treated with 1.50 moles of dry hydrochloric acid gas. While the gas was being passed in, the mixture was kept in crushed ice. After standing in the cold several hours, the solution was treated with a few crystals of the benzimido ethyl ester hydrochloride to induce crystallization and allowed to stand forty-eight hours, when it became a solid mass. This was then thrown on a filter and washed with cold alcohol and ether. It was then placed in a vacuum desiccator over calcium oxide and

[1] Die Imidoäther (1892), p. 53.
[2] Marshall and Acree: This Journal, 49, 134.

after twenty-four hours was analyzed. The yield varied from 65 to 100 per cent. The following are some typical analyses:

0.5301 gram substance gave 0.4096 gram AgCl.
0.7632 gram substance gave 0.5911 gram AgCl.
0.6166 gram substance gave 0.4777 gram AgCl.
0.6194 gram substance gave 0.4790 gram AgCl.

Per cent. chlorine,	
Found	Theoretical
19.11	19.10
19.16	.....
19.15	.....
19.12	.....

Benzimido Ethyl Ester.—As considerable difficulty was experienced in preparing pure benzimido ethyl ester by the ordinary method[1] and in keeping it pure, the following method was tried.

To an alcoholic solution of benzimido ethyl ester hydrochloride was added exactly the molecular equivalent of sodium ethylate. The sodium chloride was filtered off and the solution was distilled *in vacuo*. After several distillations a constant boiling substance was obtained, but it contained some free benzonitrile as was shown by the reaction velocity. Therefore, all solutions of the imido ester were prepared from an alcoholic solution of its hydrochloride and sodium ethylate as described under the acetimido ethyl ester.

We first proved that the free imido ester does not decompose with any appreciable velocity unless catalyzed by the ethylate. A solution of the benzimido ester hydrochloride was treated with nine-tenths of the theoretical amount of ethylate and titrated at intervals by Dr. C. N. Myers.

Time	2 hrs.	3 hrs.	22 hrs.	45 hrs.	72 hrs.	7 days	10 days	15 days	19 days
Cc. 0.2 N HCl	10.94	11.00	10.96	10.94	10.96	10.70	10.52	10.20	10.00

The amount of change due to the *uncatalyzed*, or spontaneous, decomposition of the free imido ester cannot produce any appreciable error in our constants. When portions of this

[1] Derby: This Journal, 39, 442 (1908).

solution were treated with N/8 sodium ethylate the imido ester was decomposed as usual.

Hydrolysis Correction.—In working with this compound hydrolysis was so marked that it was necessary to correct for it. This was accomplished in the following way: Amounts of benzimido ethyl ester hydrochloride dissolved in 10 cc. alcohol, corresponding to various stages in the reaction of a 0.25 N solution, were put in Nessler comparison tubes and diluted to 100 cc. with water, two drops of methyl orange being added to each tube. To another series of tubes containing 10 cc. alcohol, 90 cc. water and two drops of methyl orange were added 0.01 N hydrochloric acid till the colors matched those produced by hydrolysis in the first series.

The following table gives the amounts of 0.01 N hydrochloric acid necessary to produce this color:

Weight imido ester hydrochloride	Cc. of 0.01 N HCl	Corrected for blank
0.9280 g.	1.4	1.0
0.7424	1.2	0.8
0.4640	1.1	0.7
0.2774	0.8	0.4
0.1856	0.5	0.1
0.0928	0.4	0.0
0.0000	0.4	...

The following table gives corrections applied to the titrations at time periods corresponding to various values of x. These were subtracted from the values of x actually observed:

x	Correction in cc. 0.2 N HCl
0.00	0.05
2.50	0.04
6.25	0.03
8.75	0.02
10.00	0.01
12.50	0.00

Table I[1]—0.25 N Benzonitrile, or Imido Ester, and Sodium Ethylate

Concentration sodium ethylate	Per cent. imido ester at equilibrium	
	From nitrile	From imido ester
0.75	9.28	....
0.25	9.12	....
0.125	9.52	....
0.125	9.60	9.44 9.12
0.0625	9.86	9.76 9.60
0.03125	9.70	9.12
0.015625	9.62	9.68

Table II—0.50 Sodium Ethylate and Benzonitrile

Concentration benzonitrile	Per cent. imido ester formed
0.5 N	7.60
0.5 N	7.72
0.375 N	8.37
0.25 N	9.06
0.125 N	11.12
0.0625 N	14.08
0.03125 N	14.10

Table III—0.25 N Benzimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 10.0$
t	x	K_V
41	4.82	0.0135
51	5.69	0.0136
61	6.35	0.0134
94	8.06	0.0133
119	8.93	0.0129
132	9.32	0.0130
∞	11.36	......

Average = 0.0133

K_n = 0.1064

[1] Tables I and II are taken from another article by Marshall and Acree: THIS JOURNAL, **49**, 136, 138. The last four values for the work with the nitrile were obtained by Dr. C. N. Myers.

Table IV—0.25 N Benzimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.59$
t	x	K_V
30	3.85	0.0139
42	4.86	0.0133
51	5.54	0.0132
63	6.33	0.0130
95	8.01	0.0129
125	9.07	0.0129
156	9.82	0.0129
∞	11.32	......
	Average =	0.0132
	K_n =	0.1056

Table V—0.25 N Benzimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.25$
t	x	K_V
60	3.77	0.0677
100	5.55	0.0677
110	5.90	0.0672
125	6.42	0.0672
141	6.88	0.0668
∞	11.28	......
	Average =	0.0673
	K_n =	0.1077

Table VI—0.25 N Benzimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.42$
t	x	K_V
60	3.82	0.0686
80.5	4.73	0.0672
105	5.68	0.0666
121	6.30	0.0675
140	6.85	0.0666
162	7.43	0.0661
∞	11.30	......
	Average =	0.0671
	K_n =	0.1074

Table VII—0.25 N Benzimido Ethyl Ester and 0.03125 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.97$
t	x	K_V
72	2.56	0.00355
102	3.35	0.00343
118	3.81	0.00345
141	4.34	0.00341
170	4.97	0.00339
213	5.78	0.00334
233	6.11	0.00332
∞	11.36	....
	Average =	0.00341
	K_n =	0.1091

Table VIII—0.25 N Benzimido Ethyl Ester and 0.015625 N Sodium Ethylate

$A_1 = 25.00$	$A_2 = 0$	$K = 9.33$
t	x	K_V
100	3.67	0.00177
124	4.63	0.00184
140	5.03	0.00179
160	5.55	0.00176
180	6.18	0.00177
1260	19.74	0.00164
∞	22.58	......
Double portions used.	Average =	0.00176
	K_n =	0.1126

Table IX—0.25 N Benzimido Ethyl Ester and Sodium Ethylate

Concentration sodium ethylate	K_V	K_n
0.125 N	0.0133	0.1064
0.0625 N	0.00672	0.1075
0.03125 N	0.00341	0.1091
0.015625 N	0.00176	0.1126

Table X—Calculated Values of K_i and K_m

	Ki	K_m
$V = 8 : 16$	0.1090	0.1016
$V = 8 : 32$	0.1154	0.1007
$V = 8 : 64$	0.1193	0.0981
$V = 16 : 32$	0.1161	0.0989
$V = 16 : 64$	0.1204	0.0955
$V = 32 : 64$	0.1227	0.0906
Average,	0.1172	0.0976

Table XI—"K_n Found" and "K_n Calculated" for 0.25 N Benzimido Ethyl Ester and Sodium Ethylate

Concentration sodium ethylate	"K_n calculated"	K_n found"	Error in per cent.
0.125 N	0.1053	0.1064	+1.00
0.0625 N	0.1070	0.1075	+0.46
0.03125 N	0.1089	0.1091	+0.18
0.015625 N	0.1109	0.1126	+1.5
		Average error,	+0.78

These experiments show conclusively that the velocity of decomposition of benzimido ethyl ester by sodium ethylate can be expressed as a function of both the *concentration of the ethylate ions* and the *concentration of the nonionized sodium ethylate.* The two following tables show that sodium iodide produces a "salt effect" which is practically identical with that calculated in the manner described on page 379, by the use of our theory:

Table XII—0.25 N Benzimido Ethyl Ester, 0.0625 N Sodium Ethylate and 0.0625 N Sodium Iodide

$A_1 = 12.50$ Cor. for $NH_3 = 0$ $A_2 = 0$ $K = 9.5$

t	x	K_V
0	...	.....
73	4.30	0.00654
98	5.36	0.00654
121	6.16	0.00649
150	7.06	0.00652
166	7.50	0.00656
∞	11.30	
	Average =	0.00653
	Calculated =	0.00669

0.25 N Benzonitrile, 0.0625 N Sodium Ethylate and 0.0625 N Sodium Iodide.—Ten cc. required 3.12 cc. 0.2 N hydrochloric acid at first and 4.22, 4.23, 4.23 cc. at equilibrium. This corresponds to 8.8 per cent. imido ester present at equilibrium.

Table XIII—0.25 N Benzimido Ethyl Ester, 0.125 N Sodium Ethylate and 0.125 N Sodium Iodide

$A_1 = 12.41$ Cor. for $NH_3 = 0.09$ $A_2 = 0$ $K = 12.05$

t	x	K_V
40	4.63	0.0129
55	5.79	0.0128
77	7.06	0.0124
100	8.12	0.0123
110	8.71	0.0129
124	8.97	0.0125
∞	11.46	......
	Average =	0.0127
	Calculated =	0.0131

0.25 N Benzonitrile, 0.125 N Sodium Ethylate and 0.125 N Sodium Iodide.—Ten cc. required 6.29 cc. 0.2 N hydrochloric acid at first and 7.41, 7.38, 7.39 cc. at equilibrium. This corresponds to 9.0 per cent. imido ester present at equilibrium.

CONCLUSIONS

The experimental work and theoretical discussion in the preceding pages show that ethylates accelerate in a *purely catalytic* way the decomposition of imido esters into nitriles and alcohols and the addition of alcohols to nitriles; the velocity of the noncatalyzed reaction is so small that it can be entirely neglected. By a comparison of the reaction velocities and the conductivity data it is seen that the ethylate ions have a definite influence on the reaction which is a simple function of their concentration. The nonionized sodium ethylate, furthermore, has a definite effect on the reaction velocity which can be expressed as a simple function of the concentration of the molecules. We refer all data to the normal solution and use the expression K_i for the effect of a gram equivalent of the ethylate ions, and the expression K_m for the quantitative

action of a gram equivalent of the sodium ethylate molecules, and find practically constant values for K_i and K_m, whatever the concentration of the ethylate. For benzonitrile and benzimido ethyl ester the value $K_i : K_m = 0.1172 : 0.0976$ was found, while for acetonitrile and acetimido ethyl ester the values $K_i : K_m = 0.344 : 0.228$ were obtained.

This work proves that the purely catalytic action of sodium ethylate on the decomposition of imido esters is exactly analogous to the reaction of alkyl halides with sodium, potassium and lithium ethylates, with sodium, potassium and lithium phenolates, and with sodium 1-phenyl-3-thiourazole. In all of these cases the velocity of the reaction can be expressed as a function of the concentration of the ions increased by a function of the concentration of the nonionized molecules.

The important "salt effect," noted in so many reactions when salts are added, has been studied in all of the cases discussed and proved to be due *chiefly* to a change of the concentrations of the ions and molecules demanded by the Arrhenius theory of isohydric solutions. Small subsidiary effects may be due to the greater or smaller reactivity of double compounds formed, and to physical changes in the solution, such as variations in viscosity, double salts, ionization and electronic phenomena.

The investigation is being continued to learn if the same value for K_i is obtained by the use of potassium and lithium ethylates. The important subject of "salt catalysis" is one of the chief objects of these researches.

Johns Hopkins University
June 1, 1912

CORRECTION

In recent communications upon the relation between ionization and chemical action, under the influence of α-rays, the values given for N, the total number of ions (estimated from the data of Geiger[1], should refer to *pairs of ions*. This correction does not affect any of the general conclusions as to the equivalence of ionization to molecular action, but does necessitate a modification of the proposed mechanism of ozone

[1] P. Roy. Soc., **82**, A, 486.

formation so as to fit four instead of two ions per molecule of ozone, which change would bring ozonization into agreement with the provisions of electrolysis. This correction applies throughout my papers on ozone formation[1] and also to those upon other reactions in gaseous and liquid systems.[2]

S. C. LIND

REPORT

THE BROWNIAN MOVEMENT AND THE SIZE OF THE MOLECULES[3]

Every day we see liquids in equilibrium, and all parts of them seem to us to be motionless. If we put a denser object into them it falls, perfectly vertically if it is spherical. Finally, when it has reached the bottom of the vessel, we know that it will not rise of its own accord.

These are very familiar ideas, and yet they hold good only for the dimensions to which our organs are accustomed. It is only necessary to examine with the microscope little particles placed in water to see that each of them, instead of falling regularly, is animated by a quite irregular and very brisk motion. They come and go, wheel round, rise, fall, and again ascend without showing any tendency to rest. This is the *Brownian movement*, named after one of your fellow-countrymen, the botanist Brown, who discovered it in 1827.

This remarkable discovery attracted very little attention. The physicists who heard tell of this agitation compared it, I think, to the movement of dust which one sees with the naked eye in a ray of sunlight, the effect of air currents caused by slight inequalities in the temperature or pressure. But in this case neighboring particles move nearly in the same direction, and roughly indicate the form of these air currents. You will see, on the contrary, that the Brownian movement of two particles is completely independent, even when the distance between them is less than their diameter.

I am going to try to show you this phenomenon, one of the most beautiful which has been revealed to us by the microscope, and one which shall prove to be a faithful picture of the movement of the molecules, or, rather, we shall prove that *it is itself a molecular movement* (just as the infrared radiations are actually light).

[1] Le Radium, **9**, 104; Monats. Chem., **32**, 295; THIS JOURNAL, **47**, 397.

[2] Le Radium, **9**, 426; J. Phys. Chem., **16**, 564; Trans. Am. Electrochem. Soc., **21**, 177.

[3] Address delivered before the Royal Institution, February 24, 1911, by Professor Jean Perrin, Faculté des Sciences à la Sorbonne, Paris, and printed in the Chem. News, **106**, 189, 203, 215.

You see here on the screen a cinematograph reproduction of the movement in water of round grains of gamboge (diameter rather less than 0.001 mm.). This film was prepared by MM. Victor Henri and Comandon (Pathé film), and was kindly lent me by them. I should prefer to show you the emulsion directly, by projecting on the screen the animated view which the microscope gives of it, but the enlargement necessary would be so great that the luminosity of the projection would be too faint for this large amphitheater.

You see that in this very irregular movement it is not possible to pick out any general current drawing along several particles simultaneously. The movement cannot therefore be due to shakings of the plate which carries the droplet which is being watched, for those trepidations, when they are intentionally caused, produce precisely such currents which one sees simply superposed on the irregular agitation of the granules. Moreover, the Brownian movement persists on a thoroughly rigid structure, by night in the country as decidedly as by day in the town, on a table ceaselessly shaken by the passing of heavy vehicles (Gouy). There is not even any necessity to trouble to make the temperature of the droplet uniform. All that is gained by so doing is the suppression of currents which are perfectly recognizable, and have no relation to the irregular agitation observed. Nothing is gained either by greatly diminishing the intensity of the illuminating light or by changing its color (Gouy).

Of course, the phenomenon is not peculiar to water, but occurs in all fluids, being more marked when the fluids are less viscous, and hence especially strong in gases. In a moment I will show you the film of granules of gamboge in water; here is another which I owe to the kindness of MM. Victor Henri and de Broglie, and which shows you the Brownian movement in air of the ultramicroscopic droplets which form tobacco smoke.

In a given fluid the magnitude of the granules makes a great difference, and the agitation is the more marked the smaller the granules. This property was mentioned by Brown when he first made his discovery. As to the nature of the granules, it appears to have little if any influence. In the same fluid two granules move in the same way when they are of the same size, whatever their substance and density (Jevons, 1869). And, incidentally, this absence of influence of the nature of the granules eliminates all analogy with the displacements which a morsel of camphor undergoes when thrown on water.

Finally—and perhaps this is the strangest and most truly novel property—the Brownian movement never stops. In-

side a cell, closed so as to prevent evaporation, it can be watched for days, months, and years. It is exhibited by the liquids enclosed in quartz for thousands of years. *It is eternal and spontaneous.*

All these characteristics point to the conclusion that the granules only reveal an agitation peculiar to the fluid itself, which they do more readily the smaller they are (just as a small boat more readily feels the waves of the sea than a large one). Thus we arrive at an essential property of what is called a fluid in equilibrium; this apparent rest is only an illusion due to the imperfection of our senses, and in reality corresponds to a definite permanent regime of violent and spontaneous agitation.

I should like to tell you how this perpetual agitation derives from the second law of thermodynamics the rank of an absolute truth (Gouy, 1888), and reduces it to a law of statistics, *i. e.*, to the affirmation of probabilities which are feebler the smaller the system to which one applies them, but our time is too short, and I must at once pass to the discussion of the cause within the fluid by which the phenomenon can be explained.

To find this cause we must appeal to molecular hypotheses. You know how ancient they are, for Democritus and Leucippus, more than twenty centuries ago, knew that matter is composed of indestructible granules in incessant movement, atoms which Chance or Destiny grouped in the course of ages into the forms and substances with which we are familiar. But only tradition tells us of these early theories, and in the beautiful poem, written long after, in which Lucretius describes the atomistic views of Epicurus, I see nothing to show how these Greek philosophers were led to attribute a granular structure to matter.

It seems to me that the hypothesis might have been suggested to them by the familiar properties of mixtures. In any case there is a really serious argument in these properties which I will first discuss. For example, we all say when we have dissolved sugar in water that the sugar and water exist in the mixture, although we cannot distinguish different parts in the sweetened water. Similarly, we say that there is oxygen in the air, and, more generally, we often recognize without hesitation in the properties of a mixture those of its constituents.

This is easily understood if the substances which form the mixture subsist in it, as flowers of sulphur and iron filings exist side by side in this mixture which I am making before your eyes. You can no longer distinguish the yellow from the black grains, and the whole looks to you to have a homogeneous

gray color. You will recognize the iron, however, even from some distance, if I bring a magnet near the vessel containing the mixture; and this does not surprise you, for you know that you need only come nearer in order to distinguish the grains of sulphur from those of iron, which are in juxtaposition but are unchanged. Similarly the persistence of the properties of sugar in sweetened water would easily be explained if in this solution there are present little particles, simply mixed in juxtaposition, which by themselves would make water, and other particles which alone would form sugar. These elementary particles, or *molecules*, would be found in all mixtures in which we could detect sugar and water, and only their extreme minuteness would prevent us from seeing them individually.

Moreover, the molecules of a pure substance like water, if they exist, must be identical, otherwise they would not behave similarly when subjected to different attempts at fractionation, by boiling, for example, and the fractions successively separated would not be identical, whereas as a matter of fact they are (Dalton).

If the molecules exist, in order to understand solution and diffusion, we are forced to admit that they are in ceaseless motion. Suppose we pour alcohol carefully on to water, or superpose carbon dioxide and hydrogen (Berthollet), and leave the system at a perfectly constant temperature. You know that the two fluids gradually interpenetrate one another although the lighter may be above, and this could not occur if their molecules were motionless. When we have thus seen that the molecules of carbon dioxide diffuse into hydrogen, into oxygen, into nitrogen, and so on, it seems probable to us that they would also diffuse into carbon dioxide itself, and this amounts to saying that the molecules of carbon dioxide are in incessant motion.

This movement of the molecules also explains the pressure exercised by fluids on the walls of containing vessels, the pressure being due to the bombardment of the molecules against the walls. This explanation, worked out in the eighteenth century by Euler and Bernouilli, leads to Boyle's law, and enables us to calculate the mean velocity of the molecules of different gases (in the air of this room, for example, the molecules would have a mean velocity of about 500 meters per second). This result signalizes the first success, in modern physics, of the old hypothesis of Greek atomism.

But we are still far from a direct verification, and the supposed movements of the molecules escape us, just as the movements of the waves of the sea escape an observer who is too far away to see them. However, if a boat were in view the

same observer might see a rocking which would reveal to him the agitation of which he had no suspicion. Might not one hope similarly that if microscopic particles were present in a fluid these particles or this dust, if they were large enough to be watched under the microscope, might also be small enough to be appreciably affected by the blows of the molecules?

Now you will guess what explanation we are going to give to the Brownian movement. Every granule situated in a fluid is unceasingly struck by the molecules round it. There is no chance that these blows will exactly balance one another; our granule will thus be irregularly tossed about, and perhaps this is the Brownian movement.

This tempting explanation (Weiner, 1863) was long regarded as doubtful. In order that it may be accepted it is at least necessary that the theory should foretell the order of magnitude of the phenomenon, and as yet we do not know whether it is not immeasurably greater (or less) than our hypothesis permits.

We shall see that this quantitative verification is possible, but to arrive at it I must remind you how, some time ago, the measurement of the viscosity of gases enabled us to determine the probable size and weight of the molecules. I shall then show you that the Brownian movement, supposed to be due to the blows of the molecules, also gives a means of determining the size of the molecules. If the two results obtained by such very different methods agree, the origin of the Brownian movement will be determined.

If we admit the existence of the molecules, we are forced, in order to explain the chemical laws of discontinuity (Law of Definite Proportions, Law of Multiple Proportions, Law of Proportional Numbers), to admit with Dalton the existence of *atoms*, characteristic of the various simple substances. For then the composition of a molecule necessarily varies by discontinuous bounds, corresponding to the entrance (or departure) of at least one atom. Thus we could deduce with precision, from the phenomena of chemical *substitution*, not the absolute weights of the molecules and atoms, but the ratios of these weights.

When, for instance, calcium is dissolved in water only half the hydrogen of the water is displaced. This may be explained by assuming that the hydrogen of each molecule of water is composed of two equal parts. These parts must be indivisible by all chemical means, since no other substitution ever gives us reasons for thinking that there are more than two; these parts are called "atoms" of hydrogen. Moreover,

a molecule of water, like any mass of water, weighs nine times as much as the hydrogen it contains; thus it weighs eighteen times as much as a single atom of hydrogen. By similar reasoning it is found that a molecule of benzene weighs seventy-eight times as much as one atom of hydrogen. The weights of the molecules of benzene and of water and of the atom of hydrogen are thus in the proportion of 78 : 18 : 1. Similarly, in many cases the ratios of the weights of different molecules and atoms may be found. (Strictly speaking, all these ratios are not yet known; for instance, there is no substitution which gives the molecular weight of a simple substance like oxygen. We shall see in a moment how Avogadro's law enables us to fill up this gap.) It is very remarkable that all these determinations are concordant, so that, for example, we can mention thousands of substances from the study of which we can deduce that the atom of carbon is twelve times as heavy as the atom of hydrogen. This gives us confidence in the atomic theory, but tells us absolutely nothing about the scale of the sizes of the molecules, whether near us or infinitely distant.

We see at least that in order to arrive at the absolute weights of the different atoms or molecules, it is only necessary to know one of them. At the same time we should also get (as Helmholtz has shown) the elementary charge which one atom of hydrogen (or, more generally, one monovalent ion) transports in electrolysis. For if we knew the weight of one atom of hydrogen, we should know how many of these atoms one gram of hydrogen contains, and hence how much each carries in electrolysis, for we know that one gram of hydrogen transports about 10,000 coulombs.

Let us then try to find one of these elementary weights, that of the molecule of oxygen, for instance.

Kinetic Theory.—Suppose that a mass of oxygen occupying 1 liter (at ordinary temperature and pressure) is liquefied. The n molecules which are present in it will almost come into contact, for the liquid is nearly incompressible. Now, we know that the true volume of the granules of a heap of sand is approximately two-thirds of the apparent volume of the heap; it is therefore probable that the true volume of our n molecules is not much less than two-thirds of the volume of the liquid, and if this value is accepted there can be no very great error. A more exact theory, due to van der Waals, leads us to assume a value twice as small and to write: $n \times$ *volume of 1 molecule* = *1/3 volume of the liquid.*

On the other hand, in the gaseous state in a given volume a fixed number of molecules n collide more often the larger

they are. Or, if you prefer it, the mean free path of the molecule L is smaller in proportion as the molecules are larger or have a larger surface. Clausius and Maxwell have calculated this relation (assuming that the molecules are spherical) and have found $n \times$ *surface of 1 molecule* $= 0.7 \times$ *volume of gas/mean free path.*

If we know the mean free path we should then have, by dividing the two equations by one another, the ratio of the volume $4\pi R^3/3$ to the surface $4\pi R^2$, i. e., the radius of the molecule, and hence its volume and surface. One of these two equations, the first, for instance, would give us n, the number of molecules which form a known mass of oxygen. The mass of the molecule of oxygen will thus be obtained.

But for this we must know the free path of the molecule. Maxwell was able to deduce it from the force which is exerted by friction between two gaseous layers which slide one on the other with different velocities.

It is easy to show the existence of this "internal friction" or "viscosity." You see the jet of gas which I light at the end of this long capillary tube. If now I shorten the tube (by cutting it) the jet of gas coming from it gives a much longer flame. Thus the gas comes out more quickly from a tube of the same section. There was, therefore, a large amount of friction in the path which I have cut off, in the interior of which the cylindrical gas columns slide on one another.

The molecular hypothesis easily explains this friction. In order to understand it let us imagine two trains of passengers moving on parallel rails with almost equal velocities. The passengers could amuse themselves by jumping incessantly from one to the other, receiving a slight shock every time. Thanks to these shocks the passengers alighting on the slower train would slowly increase its velocity, while in the same way that of the quicker train would slowly decrease. The two velocities would thus be equalized as by friction if the constant difference were not maintained. The same argument applies to two gaseous layers sliding one on the other, since they bombard each other without ceasing by a transference of the molecules from one to the other.

The mathematical analysis of this simple conception, made by Maxwell, has shown that the force of friction per square cm. between two gaseous layers at a distance of 1 cm., having a relative velocity of 1 cm. per second (a force which explains viscosity), approximately satisfies the equation: *viscosity* $=$ *1/3 density $\times$ free path $\times$ molecular velocity.*

The density of the gas and the viscosity are measurable. If we can determine the molecular velocity (mean) we shall have the free path.

This last process is easy. The pressure of the gas, as we have already said, is explained by the continual bombardment of the molecules on the walls, and these shocks are the more effectual the heavier and more rapid each of them is. The exact expression, due to Bernouilli, gives: *pressure* $= 1/3$ *density* $\times$ *square of molecular velocity.* This gives the required velocity. Applied to oxygen we find about 500 meters per second at the ordinary temperature; the molecules we are breathing are moving as rapidly as bullets.

We have now only to proceed step by step; we shall have the mean free path (0.0001 mm. for air in ordinary conditions), then the molecular diameter (a molecule of oxygen is to a man very nearly as a man to the sun), then the number of molecules n to a liter (about 30,000 millions of billions), and finally the weight of the molecule of oxygen which will give us, as we have seen, all the other weights of molecules or atoms.

We find thus, the possible error being roughly 30 per cent., that the weight of 1 atom of hydrogen is only the billion-billionth part of 1.6 grams, or 1.6×10^{-24} gram. As to the elementary charge, it will be about 5×10^{-10}, or about the thousand-millionth of the charge which can be detected by an ordinary electroscope.

I am now going to tell you how, thanks to the Brownian movement, I have been able to give other means of obtaining the sizes of the molecules.

Law of Avogadro.—I have just shown you how the study of chemical substitution gives, for example, the ratio of the masses of the molecules of benzene and water, which ought to be to one another as 78 : 18. Two masses of benzene and water which are in the ration of 78 : 18 each contain the same number of molecules. Now, if we measure the volumes occupied in the gaseous state by these two masses, at the same temperature and pressure, we find that these two volumes are equal. This is not chance, and one invariably finds that two gaseous masses which contain the same number of molecules occupy the same volume when they have the same temperature and pressure. This is Avogadro's law, which may be stated as follows:

"In the gaseous state equal numbers of molecules of different substances, contained in equal volumes at the same temperature, produce in it the same pressures."[1]

[1] Avogadro's law, once well established, will give us by extrapolation molecular weights not obtained by the methods of chemical substitutions. For example, when we have found that 32 parts of oxygen or 2 parts of hydrogen produce in the same volume and at the same temperature the same pressure as 18 parts of water vapor, we know that the masses of these three kinds of molecules are to one another as 32 : 2 : 18.

You have learned elsewhere (Boyle's law) that the pressure thus developed varies inversely as the volume occupied.

These gas laws have been extended by van't Hoff to dilute solutions. We must, of course, in that case consider, not the total pressure exerted on the walls, but only that part of that pressure which is due to the blows of the dissolved molecules, the part called the osmotic pressure of the dissolved substance (which can be measured only by means of a "semi-permeable" wall, which stops the molecules of the solute but not those of the solvent). The laws of Avogadro and Boyle thus become:

"In the dilute state (gaseous or dissolved) equal numbers of any molecules whatever, contained in equal volumes at the same temperature, produce in them the same pressure. This pressure varies inversely as the volume occupied."

These laws are applicable equally to all molecules, large or small. The heavy molecules of sugar or of sulphate of quinine produce neither greater nor less effect than the molecule of hydrogen. Yet the molecule of sugar contains 45 atoms, and that of sulphate of quinine more than 100, and it would be easy to find other more complex molecules which obey the laws of van't Hoff (or those of Raoult which follow from them).

Is it not then conceivable that there is no limit of size for the assemblage of atoms which obeys these laws; is it not conceivable that even visible dust also obeys them exactly, so that a granule agitated by the Brownian movement has neither more nor less effect than a molecule of hydrogen, as regards the action of its bombardments on a wall which stops it? Or, more briefly, is it unreasonable to think that the laws of perfect gases may be applied also to emulsions composed of visible grains?

I have made this assumption, and it is in this direction that I have sought a crucial experiment which would decide the origin of the Brownian movement, and at the same time would either provide or preclude an experimental basis for the molecular theories.

The following appears to me to be the simplest:

The Distribution of Equilibrium in a Vertical Column of Diluted Matter.—You know that the air is more rarefied on mountains than at sea level, and that in a general way a column of gas is compressed under its own weight, the state of equilibrium resulting from the conflict between the force of gravity, which makes the molecules fall, and their movement, which scatters them incessantly.

The law of rarefaction formulated by Laplace (to show how the altitude can be deduced from the barometer) follows of

necessity from Boyle's law, and can be enunciated as follows:

Every time that one ascends a fixed distance, the density is divided by the same number. Or, more briefly, equal vertical elevations are accompanied by equal rarefactions.

For example, in air at the ordinary temperature the density diminishes by one-half each time one ascends 6 kilometers (it is immaterial from what level).

But the elevation which produces a double rarefaction would not be the same in hydrogen. A simple process of reasoning shows that the way in which the nature of the gas influences the result is a necessary consequence of Avogadro's law, and may be enunciated as follows:

The elevations which produce the same rarefaction for two different gases (at the same temperature) are inversely proportional to the weights of the molecules of these gases.

For instance, if in oxygen at 0° it is necessary to rise 5 km. to make the density twice as small, it would be necessary to rise 80 km. in hydrogen at 0°, since the molecule of hydrogen is 16 times as light as the molecules of oxygen.

You see here a diagram showing three huge vertical cylinders (the largest is 300 km. high) into which the same number of molecules of hydrogen, helium and oxygen have been placed. At a supposed uniform temperature, the molecules would distribute themselves as the diagram shows, collecting more towards the bottom the heavier they are.

Now we have been led to believe that the laws of perfect gases are possibly applicable to emulsions. If this is so, and if we make an emulsion in which the grains are equal, the distribution of matter in a vertical column of this emulsion ought to be the same as in a gas. In other words, once arrive at the distribution of equilibrium and then equal elevations will be accompanied by equal rarefactions. But if it is necessary to rise only 0.05 mm., i. e., 100 million times less than in oxygen, for the concentration to become twice as small, then we must conclude that each grain of the emulsion weighs 100 million times more than one molecule of oxygen. This last weight could be ascertained if we could weigh the grain, which would be a stage between the molecular dimensions and those which are in our scale.

Of course the effectual weight of this grain would be the difference between its real weight and the thrust it would undergo in the liquid (according to Archimedes' principle). If the granules were lighter than the intergranular liquid, they would accumulate in the upper layers (equal depressions would produce equal rarefactions). They would distribute

themselves uniformly if they had the same density as the liquid.

Practical Realization.—To test these results I used the emulsions which are obtained by precipitating alcoholic solutions of resins with water. Thus, as you see, we get with gamboge a beautiful yellow liquid, with mastic a white liquid like milk. The microscope reveals in these liquids the resin precipitated in the form of *solid* round granules, which do not agglutinate when the chances of the Brownian movement bring them into contact (which is what happens with other resins which give soft granules).

But the diameters of these granules are very varied, and I had to sort them so as to get emulsions in which all the grains were nearly the same size. The method I employed may be compared to the fractionation of a liquid mixture by distillation. Just as during distillation, the parts first vaporized are relatively richer in volatile constituents, so during the centrifugation of an emulsion the portions first deposited are relatively richer in large granules. Thus you will see that it is easy to find a practical method of sorting the grains according to their size by fractional centrifugation. The operation is long (I spent some months over it), but it only requires patience.

Once get an emulsion with sufficiently uniform granules, and then the mean weight of the granules must be determined. Their density is measured like that of any other powder (the weight of resin in suspension in the flask used is determined by simply drying). The only difficulty is then to determine the diameter. The obvious way seems to be to measure it with a microscope by the clear chamber method by means of a micrometer objective. But the granules used are so small that errors of 20 per cent. or more might easily be made. A method which is almost as direct consists in allowing a droplet of the emulsion to evaporate on the micrometer objective; it is found, as you can see here on a projection, that the granules then arrange themselves in regular lines, the length of which could be measured with a fair degree of accuracy. Dividing this length by the number of granules gives the diameter.

Another long but more accurate method consists in counting how many granules there are in a known volume of the standardized emulsion, which gives the mass of a granule, and hence its radius, since we know the density. For this method I used the fact, accidentally observed, that in a feebly acid medium the grains of gamboge adhere to the glass. At an appreciable distance from the walls the Brownian movement is not modified, but as soon as the chances of this movement bring a grain into contact with a wall, the gran becomes motionless.

The emulsion thus gets progressively weaker, and after some hours all the granules it contained are fixed. One can then count at one's leisure all those which come from a cylinder of arbitrary base (measured by the clear chamber).

Finally, a third method, which I shall not explain to you in detail, is based on the observation of the time necessary for the upper portion of a vertical column of emulsion (several cm. high) to clarify to a given height. This time, required by the granules to descend on the average from this height, gives the diameter by applying the law of the fall of a sphere in a viscous fluid (Stokes).

These three processes agree, and this must be so to give us confidence in the accuracy of the measurements of a radius which is less than a thousandth of a mm.

Method of Observation.—We must now get an arrangement which will enable us to ascertain the distribution of equilibrium as a function of the height. For this purpose a drop of emulsion is placed in a shallow tank, the depth of which is 0.1 mm.; the drop is at once flattened out by a cover slip which closes the tank and the edges of which are paraffined to prevent evaporation.

The tank can be arranged vertically, the body of the microscope being horizontal, and thus the vertical column throughout which the emulsion can distribute itself may be made some mm. high. It will be seen that the grains accumulate in the lower layers, and tend to give rise to a distribution of equilibrium (practically reached after one or two days), in which the progressive rarefaction as a function of the height is manifested as you can see in the projection, which plainly recalls the law of rarefaction of heavy gases.

But however small our granules are, they are so heavy that the rarefaction is very rapid, and the height over which measurements can usefully be made is less than 0.1 mm.

The tank can also be made horizontal, the body of the microscope being vertical, in which case only about a quarter of an hour is necessary for equilibrium to be established. The objective of the microscope, of great enlarging power, has only a small depth of field, and we can only see clearly, at the same instant, the granules situated in a very thin horizontal layer, the thickness of which is only a little over 0.001 mm. If the microscope is raised or lowered one sees the granules of another layer. The distance between these two layers may be deduced from the vertical displacement read on the screw of the microscope; the ratio of the number of granules perceived gives the rarefaction corresponding to a known elevation. It was with this apparatus that I made my first experiments.

I was not sure that there would be the least rarefaction, and moreover, not even sure whether, on the contrary, all the granules would not group themselves quite against the bottom. But I saw that a permanent state of uniform rarefaction was established. This rarefaction is specially striking when, keeping the eye fixed on the preparation, the observer rapidly raises the microscope by means of its micrometer screw. The granules are then seen to be rapidly rarefied, like the atmosphere round an aerostat which is rising.

It now remains to make accurate measurements. When one sees in the field some hundreds of granules which are moving in all directions or which disappear while new ones make their appearance, one soon gives up trying to count them. Luckily we can take instantaneous photographs of the different layers, and then at our leisure count the number of granules in these layers on the plates.

It is thus easy to verify that equal elevations are accompanied by equal rarefactions. For instance, for granules of radius equal to 0.212μ three successive rises of 30μ practically lower the concentration to one-half, one-quarter and one-eighth of its value. With other grains of radius equal to 0.367μ an elevation of 6μ is enough to make the density about twice as small.

To obtain the same rarefaction in air we have seen that it would be necessary to rise 6 km., a thousand million times as much. If our theory is correct, the weight of a molecule of air would be the thousand-millionth part of the weight of one of our granules in water. The weight of the atom of hydrogen would be obtained in the same way, and now our interest centers on finding out if we shall thus obtain the same numbers as those given by the kinetic theory.

So I was much elated when I found at the first attempt numbers which were the same as those obtained by the kinetic theory, i. e., by a fundamentally different method. I also varied the conditions of the experiment as much as I could. For instance, the mass of my granules had a series of values ranging between limits which were to one another as 1 : 40; I changed the nature of the granules, using different resins (especially mastic); by the addition of glycerol I increased the viscosity of the intergranular liquid in the ratio of 120 : 1, at the same time changing the nature of the liquid; finally, I made a considerable change in the apparent density of the granules, which, in water, varied from the same to five times as much, and which became negative for gamboge in glycerol

with 10 per cent. of water (in this last case the granules being lighter than the liquid accumulated in the upper layers).[1]

I always obtained concordant results, giving for the atom of hydrogen a weight very nearly equal to the value 1.6×10^{-24}, given by the kinetic theory.

I do not think this agreement can leave any doubt as to the origin of the Brownian movement. To understand how striking it is it must be remembered that before the experiment one could not have dared to affirm that the fall of concentration would not be negligible for such a small height as a few microns, or that all the granules would not collect in the immediate neighborhood of the bottom of the tank. The first eventuality would give a zero value, and the second an infinite value for the weight of the hydrogen atom. That one should have hit exactly upon a value so close to that foretold, with *each* emulsion, in the *enormous* interval which seems *a priori* possible, could obviously not be a chance coincidence.

But there is more to be said. While the kinetic theory, because of the simplifications permissible in its calculation, gives results of an uncertain degree of approximation, even from perfect experiments, the numbers given by emulsions correspond to a true measure, such that there is no limit to its accuracy. By this method we can readily weigh the atoms, and not only roughly estimate their weight.

The two series of experiments which I regard as the most accurate have thus given me for the weight of the atom of hydrogen (after the enumeration of about 30,000 granules) the value 1.47/1,000,000,000,000,000,000,000,000, or more briefly 1.47×10^{-24} grams.

The sizes of the other molecules can be derived from this. For example, you will easily see that there must be in each cc. of air (in normal conditions) thirty-one thousand millions of thousand millions of molecules, and that the elementary charge or electron must be 4.2×10^{-10} (C. G. S. electrostatic units).

The Sizes of the Molecules can be Deduced from the Degree of Agitation.—Thus we have extended the laws to emulsions with much success, and at the same time obtained the absolute weights of the atoms. It is remarkable that in these measurements we have not had to concern ourselves about the activity of the Brownian movement. The laws of gases are verified by emulsions equally well in glycerol, in which the Brownian movement is hardly perceptible, and in water, in which

[1] Quite recently, under my direction, M. Bruhat made the temperature vary from —10° to +58°, and still found the same weight.

it is very brisk, the only difference being that the distribution of equilibrium occurs much more quickly in water than in glycerol.

On the other hand, this Brownian movement, when studied by itself, will give us a new method of determining the size of the molecules, perhaps less intuitive than the preceding method, but just as accurate; it was suggested by Einstein in an admirable theoretical article (1905).

Without trying to follow the infinitely complicated path which a granule describes in a given time, Einstein considers only its displacement during that time, i. e., the rectilineal segment which joins its starting point to its final position, and shows that if certain fundamental hypotheses of the kinetic theory are correct, the knowledge of the *mean* value of this displacement enables us to determine the sizes of the molecules.

I cannot now give the details of this argument, and must confine myself to saying that the principal hypothesis used by Einstein consists in supposing not only, as has already been done, that at the same temperature all the molecules have the same mean energy of movement, but that even a perceptible granule has the same mean energy of movement. Then Einstein's formula gives this mean molecular energy, since we know the mean displacement in a given time, in a liquid having a known viscosity, of spherical granules of known radius. The molecular energy can be obtained thus, and at the same time the masses of the different molecules, for we have seen that we know what must have been their velocities in order that their bombardments on the walls might explain the pressures observed.

Einstein pointed out that the order of magnitude of the displacements observed agreed perfectly with the theory, and left to the experimenters the task of making a more precise comparison. Since I had rough granules of known diameter, I was in a position to make this comparison, as M. Langevin pointed out to me when he told me of Einstein's theory, of which I was then ignorant. I first entrusted the measurements with gamboge to M. Chaudesaignes and with mastic to M. Dabrowski, and then I myself plotted the positions. The result was decisive and showed the rigorous exactitude of Einstein's formula, the weight of the atom of hydrogen calculated by this method being 1.45×10^{-24} gram, practically identical with the number which the distribution in height of the emulsions gave me.

You see on the screen here, enlarged so that sixteen divisions represent 50 microns, three diagrams obtained by trac-

ing the segments which join the consecutive positions of a single granule of mastic of radius 0.52μ, marked at intervals of 30 seconds, with a clear chamber. It was by taking the mean of similar segments that Einstein's formula was verified.

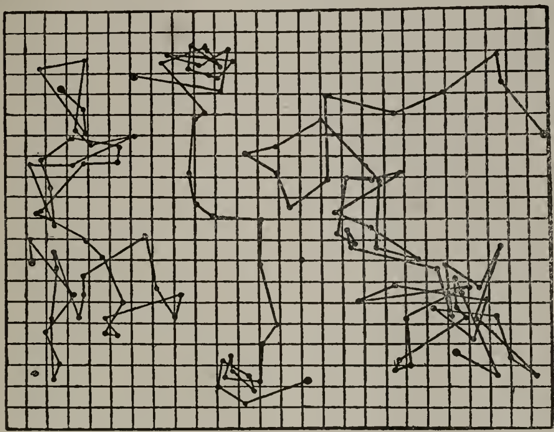


Fig. 1

These diagrams, however, give you only a very feeble idea of the enormous complexity of the actual trajectory. If, for instance, the positions were plotted at the end of each second, each of these rectilineal segments would be replaced by a polygon of thirty sides, relatively just as complicated as the diagram here reproduced, and so on.

To vary these conditions I succeeded in preparing granules much larger than those which I had used up to the present. For that purpose I allowed water to fall slowly on an alcoholic solution of mastic, by a funnel with a drawn-out tube. The granules which are formed in the zone of passage have usually a diameter of a dozen microns, a diameter which is measured directly in the clear chamber, and they are then about 100,000 times heavier than the smallest I used. In order that this weight should not keep them constantly in immediate contact with the bottom, I observed them in a solution of urea which has almost the same density as theirs. I have thus shown that Einstein's formula is still applicable. Finally, I proved

another formula, also deducted by Einstein from the molecular hypotheses, which relates to the mean rotation of a granule in a given time. This formula foretelling about 100° of rotation per second for granules of the order of a micron would appear to be difficult to verify. But, luckily, I had large granules; owing to the size of these grains, and because some of them contained little enclosures which act as marks, *I have been able to demonstrate and measure their rotation.* The measurements, as yet not very accurate, gave me 1.56×10^{-24} as the weight of the atom of hydrogen, so that there is no doubt about the applicability of this new method of arriving at the size of the molecules.

I have nothing more to tell you about my researches, but you will at least allow me to mention other quite recent methods, which also enable us to determine the sizes of the molecules. One of them, due to Lord Rayleigh, gives the number of molecules contained in a column of air of calculable mass, from the diffraction which they cause in solar light, and which, favoring the most refrangible colors, is the origin of the *blue of the sky.*

To determine the size of the molecules it is thus only necessary to measure at the same time, for the same radiation, the light of the sun and in a known direction that of the sky. The measurements (Bauer and Moulin), which do not allow of great accuracy, because of the difficulty of calculating the part which the rays reflected from the ground take in the illumination of the sky, nevertheless give the order of magnitude very fairly, indicating within about 50 per cent. 1.6×10^{-24} for the weight of the atom of hydrogen.

Another more accurate method is based upon the measurement of the electric charges transported by microscopic droplets. These charges are generally small, and are integral multiples of an atom of electricity, thus directly measurable, which is equal to that which an atom of hydrogen can transport in electrolysis. As the amount transported by 1 gram of hydrogen is known, we have thus the weight of the atom. This method, suggested by Townsend and Sir J. J. Thomson, and perfected by H. A. Wilson, and especially by Millikan (who succeeded in proving very definitely the atomistic structure of electricity), actually gives numbers lying between 1.4×10^{-24} and 1.7×10^{-24}.

Another group of measurements has its origin in the properties of radioactive substances. You know that some substances emit α rays which make zinc sulphide phosphoresce. Sir William Crookes, examining this phosphorescence under the microscope, saw that it resolved itself into a swarm of

scintillations extinguished as soon as they appeared. The rays which excite them are material, for wherever they penetrate the presence of helium may be proven (Rutherford); they are probably formed by atoms of helium positively charged. Sir William Crookes supposed that each scintillation marked the arrest of one of these atoms, which are hurled out with the enormous velocity of 20,000 km. per second. If then the number of scintillations due in a given time to a known mass of radioactive substances is counted, and if we measure the volume of helium liberated in the same time, we know how many atoms this volume contains, and the size of the molecules follows from it. We can also (I do not lay stress on this point, simply for want of time) measure the positive charge radiated or the fraction of the radioactive substance destroyed. These wonderful experiments give for the weight of the atom of hydrogen numbers lying between 1.4×10^{-24} and 1.6×10^{-24}.

I can only mention to you the existence of the beautiful theories by which Planck and Lorentz have connected the size of the molecules with the distribution of energy in a spectrum of an incandescent substance. The measurements, which may be made very accurate, now give for hydrogen the weight 1.6×10^{-24}.

I think you will be struck by the diversity of the ways which thus lead to the same result. If our hypotheses are false, each of these phenomena could give any range of values lying between zero and infinity. For instance, as regards the Brownian movement, the measurement of the mean displacement would give numbers differing for large and small granules. These values would, moreover, bear no relation to those, equally variable, given by the distributions in height. The fact that there is convergence, not only in each method, but in all the methods, that phenomena as fundamentally different as the viscosity of gases, the Brownian movement, the blueness of the sky, the electrification of droplets, radioactivity, the distribution of energy in the spectrum, all show the discontinuity of matter, and give the same magnitudes for the elements of matter, *these facts demonstrate the objective reality of the molecules*. Perhaps you will also find that this marvelous agreement gives you a good example of the satisfaction that the love of the beautiful finds in the study of the sciences.

JACOBUS HENRICUS VAN'T HOFF. Sein Leben und Wirken. Von ERNST COHEN, Professor an der Reichs-Universität zu Utrecht. Mit 2 Gravüren und 90 Abbildungen. Grosse Männer, Studien zur Biologie des Genies. Herausgegeben von WILHELM OSTWALD. Band 3. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. S. xv + 638. Preis: geh., M. 14.75; geb., M. 16.

A large number of biographical sketches of van't Hoff have recently appeared. Most of these were *in memoriam* notices and very, very brief and incomplete. When such a man appears in any branch of science it is well that he should have a competent and willing biographer, since the perusing of such a life often stirs the instinct of young men and women to do something themselves.

Van't Hoff has been very fortunate in this respect, in that his assistant and friend—Cohen—has both a skilful and willing pen, and this work is literally a labor of love.

The book deals with the life of van't Hoff in periods. The first period has to do with his youth, the second with his student life, and his "Wanderjahre." The third period discusses his return to Utrecht, and his earlier investigations, especially in the field of stereochemistry. Letters to van't Hoff during this period show the reception of this work on the part of a number of the leading chemists.

Van't Hoff's Amsterdam period is treated in five sections. The period from 1877 to 1884 marks the beginning of his work in this important university. The second period, 1884–1885, has to do especially with the publication of his "Etudes de dynamique chimique."

The third period, 1885–1887, was the one in which the relation between gas pressure and osmotic pressure was pointed out, and to account for certain exceptions to this relation, the theory of electrolytic dissociation was proposed by Arrhenius.

The fourth Amsterdam period (1887–1894) was characterized by great development in the field of general chemistry, being largely applications of the generalizations already reached by van't Hoff. The last Amsterdam period, 1894–1896, was not marked by the same activity as the earlier.

In 1896 van't Hoff was called to the University of Berlin and accepted the call. His work while in Berlin, especially in connection with the Stassfurth salt deposits, is too well known to call for special comment in this brief review.

The long and close relation of Cohen to van't Hoff, his admiration for his teacher and colleague, and the literary skill

of the author of this book in presenting things in an attractive form, make this an authoritative and very readable treatise on the life and work of one of the truly great men of science of his day—of one of the very greatest chemists of all time. H. C. J.

DIE EXISTENZ DER MOLEKÜLE. Experimentelle Studien von THE. SVEDBERG, Professor an der Universität Upsala. Mit 4 Tafeln und 76 Abbildungen im Text. Leipzig: Akademische Verlagsgesellschaft. S. 243. Preis: brosch., M. 12.00; gebunden, M. 13.20.

As the author says in his preface, this book deals chiefly with his own experiments, the work of other investigators being alluded to only as it has a bearing upon his own. He seeks to obtain experimental evidence of the existence of molecules as discrete entities.

The first part of the book is made up of a very full account of a long series of experiments on the colors of colloidal and true solutions, the larger part of the matter consisting of numerical tables and series of observations. In the opinion of the reviewer these could have been left out, or at least expressed in graphical form only, as they are bulky and not very readable.

The author reasons as follows: If a colloidal solution, in which the material can be seen with the microscope to exist in a state of very fine subdivision, shows certain properties, such as color produced by absorption, and these properties pass by gradual transitions to the properties shown by true solutions, *as the size of the particles is reduced* by appropriate means, we have strong evidence that even in the true solutions the dissolved matter is present in a state of fine subdivision (molecules) and not uniformly distributed (i. e., continuous). He investigates the phenomenon by a colorimetric method and also with the spectrophotometer, studying colloidal solutions of gold, ferric oxide, arsenous sulphide, selenium, indigo, aniline blue, indophenol and azobenzene.

In some cases the absorption increases as the size of the particles is diminished, reaching its maximum value in the true solution. In other cases, azobenzene, for example, the reverse is true.

In the opinion of the reviewer, these experiments do not furnish much evidence for the existence of molecules. The action of very small bodies upon light waves is so dependent upon their size, and so little understood, that experiments of this nature can be interpreted only with difficulty. Granular deposits of metallic sodium and potassium formed by heating the metals in exhausted bulbs show all colors of the

rainbow in transmitted light, the color appearing to depend upon the size of the small metal particles. Granular deposits of selenium and some of the aniline dyes behave in the same way.

Professor Svedberg's argument that if the properties of colloidal solution in which the microscope reveals small particles can be made to pass gradually to the properties of a true solution, by reducing the size of the particles, then the true solution must contain still smaller particles (i. e., molecules), does not appear to be quite free from objection. It seems conceivable that the same might be true if, in solutions, the substance dissolved was continuous. In the second part of the book the author deals with diffusion phenomena, and here his arguments are much more convincing. He compares the rates at which substances in the colloidal form diffuse into pure water, as dependent upon the sizes of the particles, and compares them with the rate at which the dissolved substance diffuses. If the same law is followed in each case, it is a strong argument for the existence of molecules. His investigations of the sizes of molecules of certain organic compounds by this method is especially interesting.

By the study of diffusion he calculates the sizes of the particles in colloidal solutions, and compares them with the sizes observed with the ultramicroscope. The diffusion experiments certainly give strong support to the molecular theory.

The author makes no mention of the recent work of van Calcar and Lobry de Bruyn, who showed that centrifugal force alters the concentration of a solution, and may even, in the case of a saturated solution, cause crystallization along the periphery of the centrifuge. Such a separation could scarcely occur if the specific gravity were constant in every infinitesimal element of volume, as would be the case if the dissolved substance were continuous.

Absorption and diffusion belong to the class of multimolecular phenomena, as the author calls them, since their study is associated with the observation of effects produced by large numbers of molecules. Of greater extent is the paucimolecular class which is next considered, for here we deal with effects produced by a few molecules or in some cases by a single molecule.

The author draws attention to the following phenomena, all of which, with the exception of the first, have been discovered since 1903:

1. The "Brownian" movement of small particles in suspension, which is now definitely ascribed to the circumstance that

for very small particles the resultant force of the molecular impacts from all sides is not zero. Particles of smoke, suspended in air, are shown by the microscope to be in violent agitation, as the result of the molecular bombardment to which they are subjected. In a gas, in which the molecules are moving according to the kinetic theory, there will be moments at which a given minute volume will contain more molecules than at others, in other words, the density of the gas will vary from point to point. If a smoke particle lies between a region of high and a region of low density, it will move towards the latter, as a result of the greater pressure exerted on one side. This, of course, amounts to the statement that the resultant force of the impacts is not zero, given below.

2. The "scintillation" of zinc sulphide produced by the impacts of α particles from radium (Crookes).
3. The ionization of a gas produced by the passage of a single α particle through it, discovered by Rutherford.
4. The photographic records of the impacts of single α particles upon photographic plates (Kinoshita).
5. Wilson's experiments for showing the tracks of single α particles by condensing water vapor on the ions formed in their paths.
6. The variations in the ionization current observed by Meyer[1] explained by departures from the "mean free path" of the kinetic theory.
7. The observations of Svedberg on the spontaneous concentration variations in radioactive solutions and gases.

Of the above phenomena the first and the last are the only ones to which the author devotes much space. The description of his experiments on the Brownian movement requires two hundred pages, nearly one-half of which are devoted to numerical tables of observations.

The spontaneous concentration variations of colloids are investigated and the movements of the individual particles studied by photographic and other methods, and the results compared with the theories developed by Einstein and v. Smoluchowski. The effects increase as the size of the particles is diminished, and are in perfect accord with the molecular kinetic theory.

The last portion of the book is devoted to the spontaneous concentration variations which occur in radioactive solutions and gases (radium emanation, for example).

The solution in the form of a thin film is brought in close proximity to a screen of phosphorescent zinc sulphide under

[1] Physik. Z., **11**, 215 (1910).

the microscope, and the scintillations resulting from the bombardment by α particles observed. In this way the space distribution of what we may term the "exploding" radioactive molecules in the solution can be studied. A similar method is used with the emanation.

We have, as yet, no experimental means of detecting the variations of concentration in solutions except in the case of radioactive substances. There is no doubt but what they occur, in fact they must occur if the molecules of the dissolved substance are moving about, in a manner analogous to the density variations of gases referred to previously.

The book could have been made more interesting by condensation, and by the omission of most of the numerical tables of observations. R. W. W.

ATOMPROZENTE UND GEWICHTSPROZENTE, sowie die Methoden zu ihrer gegenseitigen Umwandlung. Ein metallographischer Beitrag zur graphischen Technik der physikalischen Chemie. Von DIPL.-ING. FRITZ HOFFMANN. Ingenieur der Berndorfer Metallwarenfabrik Arthur Krupp, Berndorf (Nieder-Oesterreich). Halle a. S.: Verlag von Wilhelm Knapp. 1912. pp. 20. Price, M. 1.80.

In the study of the alloys for the purpose of determining the presence or absence of definite metallic compounds, it is necessary to know the atomic relations of the elements rather than the weight relations. The author has illustrated three methods of changing weight percentages into atomic percentages: (1) A mathematical method. (2) A combined mathematical and graphic method. (3) A purely graphical method. The graphical methods are explained by numerous diagrams.

The monograph should be of value to anyone working in the field of heterogeneous equilibria, especially if three or more components are involved. ROBERT S. WILLIAMS

DIE ELEKTROCHEMISCHE INDUSTRIE FRANKREICHS. Von M. R. PITAVAL, Ingénieur-Directeur, ins Deutsche übertragen von DR. MAX HUTH, Chemiker der Siemens & Halske A.-G., Berlin. Mit 35 in dem Text gedruckten Abbildungen. Monographien über angewandte Elektrochemie. Herausgegeben von VIKTOR ENGELHARDT. XLII Band. Halle a. S.: Druck and Verlag von Wilhelm Knapp. 1912. pp. viii + 140. Price, M. 9.00.

The French author, well known through his reviews upon the progress in the electrochemical industries of France, has brought together, in compact form, their present status. The chlorine industry receives 12 pages, calcium carbide 12, fixation of atmospheric nitrogen 17, and the metals 68. Of the last, the aluminium industry alone has 15 pages, copper 10, and steel 27.

The book has the good points of most French technical pub-

lications, logical arrangement and clear exposition of the subject; it has also the unwelcome feature of not giving the sources whence the information has been derived. The reader has no means of knowing how much reliance can be placed upon the several statements; he is forced to look for other sources and make comparisons before he can accept the figures.

That the publication of the book is one of the well-known collection of monographs upon Allied Electrochemistry edited by V. Engelhardt is in its favor; it shows that European electrochemists, familiar with the work in France, think favorably of the treatment of the subject. The translator does not seem to appear familiar with German metallurgical terms, e. g., on page 88 "Matten" is a germanization of the French "mattes;" the corresponding German word is "Steine."

H. O. HOFMAN

ABSTRACT-BULLETIN OF THE PHYSICAL LABORATORY OF THE NATIONAL ELECTRIC LAMP ASSOCIATION, Cleveland, Ohio. EDWARD P. HYDE, Director. January, 1913. Vol. 1, No. 1. Cleveland: The Physical Laboratory of the National Electric Lamp Association. 1913. pp. viii + 127.

The purpose of this publication is best expressed in the words of the Director of the Laboratory:

"The Physical Laboratory of the National Electric Lamp Association was organized in the autumn of 1908 for the development of those branches of science with which the art of lighting is closely associated. Up to the present time, sections in physics, physiology and psychology have been organized.

"The results of the investigations carried out in this laboratory have been presented before the various scientific and technical societies of the United States, and have been published in the proceedings of those societies and in the recognized scientific and technical journals of this country and Europe. It has seemed unwise to restrict the publication of these investigations to a new journal issued by the Laboratory, or to reproduce the published papers in full in such a Laboratory bulletin. And yet it has seemed advisable that the complete work of the laboratory should be collected in such a way as to render it available to all who may be interested.

"To this end the present *Abstract-Bulletin* is being published and distributed. This *Abstract-Bulletin* contains an abstract of every research carried out in the laboratory from its inception to the summer of 1912. The abstracts, written by the authors of the original papers, are fully illustrated with photographs and drawings, in the hope that to all, except those

specially interested in the details of the investigation, they may be satisfactory substitutes of the original papers.

"Subsequent numbers of the *Abstract-Bulletin* will be issued as the further accumulation of published investigations may warrant."

To the reviewer this seems a step in the right direction. Taking the field of chemistry alone, the literature has grown to such an enormous bulk and is yearly increasing to such an extent, the multiplicity of journals is such, that no one, however narrow his field, can hope to be able even to glance through all the journals which may contain articles of value to him, to say nothing of subscribing to them, and it is taxing even the best-equipped libraries to keep up with the rising flood. The necessity of abstract journals is therefore recognized by every one. And who is better qualified to prepare an abstract than the author of the original article himself? Of course, the tendency in such a case is to make the abstract too long, but this ought to be easily overcome by judicious editing. This plan of abstracts by authors would ensure better and more accurate work, would relieve the various societies already publishing abstract journals of great expense and would allow many men now giving much of their time to abstracting to apply their energies to more productive work. But the question arises, How many abstract journals are we to have? Every duplication is, of course, a waste of time, money and effort. Until the millenium of a universal language is reached, it will probably continue to be necessary to have an abstract journal in, say, English, German, French and possibly Italian, for a large majority of those to whom an abstract journal is most useful, viz., those not having access to a large library, have neither the time nor opportunity to master another than their native language. But why could not an International Association of Chemical Journals be formed which should limit the publication of abstract journals by its members to one in each language, and require that all original papers submitted for publication be accompanied by a brief abstract, a copy of which could be sent to each of the four or five abstract journals? The cost of translation of such abstracts would be negligible as compared with the present system, errors would be reduced to a minimum, the abstracts could be published immediately after the appearance of the original and every reader could get a journal which was published in the language most useful to him. C. A. R.

Explosives. A Synoptic and Critical Treatment of the Literature of the Subject as Gathered from Various Sources. By Dr. H. Brunswig, Translated and Annotated by Charles E. Munroe, Ph.D., LL.D., and Alton L. Kibler, M.S., Ph.D., George Washington University. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1912. pp. xv + 350.

This book is a notable contribution to the literature of explosives; its scope can hardly be better stated than in the following extracts from its preface: "The indefatigable labor of decades in the manufacture and use of explosives has yielded rich experimental material which is still waiting a thorough working over and coördination in accordance with scientific laws. * * * The development of our knowledge of explosive processes forces us more and more into the narrow field of an exact chemistry of explosives, or, in other words, a physical-chemical science dealing with the velocities of chemical reactions and chemical equilibria at very high temperatures and pressures. * * * It seems a worthy task to gather together the facts recorded in the literature of explosives, arrange them in accordance with the physical-chemical views, and take a survey of the present status of the chemistry of explosives and its most important aims. * * * Theoretical-mathematical discussions have been carefully omitted in the following pages. * * * We have made use of only such experimental facts as are found in the literature within every one's reach."

In accordance with this program the book is divided into two parts, the first considering the conditions governing explosive reactions; the influence of surrounding circumstances on the initial velocity of reactions and of propagation, including temperature, pressure and catalytic influences; the rate of increase and the maximum of the pressure developed; the temperature of explosions; the influence of pressure and temperature on the gases developed by explosive reactions; the velocity and intensity of explosions by influence; and the flame of explosions, especially of interest in connection with fire-damp problems.

The second part of the book treats of the characteristics of particular explosives and of the various modes of igniting them. They are classified according to their uses as propellants or for blasting purposes. For each variety its history, its composition, its preparation and its properties are treated. Nearly one-third of the book is devoted to this branch of the subject, and several tables facilitate the comparison of the different types. Cautions on the handling and, when necessary, on the destruction of explosives are given, with details of some important works accomplished by their

aid. Convenient indices of authors mentioned in the text, and of the many subjects treated, complete the work.

In fine, the book supplies information long needed both by theoretical scientists and by practical technologists. The authors are to be congratulated for supplying a need long felt.

HENRY L. ABBOT

A MANUAL OF CEMENT TESTING, for the Use of Engineers and Students in Colleges and in the Field. By WILLIAM ALLYN RICHARDS, B.S. IN M.E., Instructor in the University of Chicago, and HENRY BRIGGS NORTH, D.Sc., Associate Professor of Chemistry in Rutgers College. Illustrated. New York: D. Van Nostrand & Co. 1912. pp. x + 137. Price, $1.50.

This little book was written as a laboratory guide for students in the engineering courses of our schools and universities and its style and arrangement are extremely elementary. It may, however, prove helpful to inexperienced cement testers in field laboratories when they have not learned the rudiments of the various principles involved. The object claimed for it is to promote greater uniformity in cement testing and the various steps of procedure are explained in detail. It has been compiled from the standard treatises on cement testing and full credit is given at the end of each chapter.

The book is divided into two parts and appendix. The first part describes the methods used in the physical testing of cement and the various aggregates used with it; the second part treats of the chemical analyses of the above and the appendix is a reprint of the standard specifications and uniform methods of testing and analyses as adopted by the principal engineering societies.

The methods for chemical analysis are most too academic for the practical cement chemist but, by following the instructions given, little error will enter into his determinations.

The paper and binding are good, the type large, clear and well spaced. Forty-six illustrations of fair quality are included in the text.

C. N. WILEY

AUSFÜHRUNG QUALITATIVEN ANALYSEN. Von WILHELM BILTZ. Mit 1 Tafel und 13 Figuren im Text. Leipzig: Akademische Verlagsgesellschaft m. b. H. S. xi + 139. Preis: brosch., M. 5.00; geb., M. 6.00.

This little book on Qualitative Analysis differs from most of its predecessors in that its author's purpose has been to show how the constituents of a mixture may be determined as quickly as possible, and with reasonable accuracy, rather than to lay particular stress on the detection of very small quantities or to make the qualitative study of the metals serve as a reason for the introduction of a mass of information

about each element. Nearly one-third of the book is devoted to "Dry Reactions." The author feels that these tests should not be classed as preliminary, to be used or not at the discretion of the analyst, but that they should form an integral part of the scheme and in certain cases should replace the usual wet methods. This part of the book seems to be given undue emphasis from the view point of the general analyst to whom dry reactions cannot be as helpful as they are to the mineralogical chemist. The scheme of wet analysis is about the usual one but contains no equations and very few reasons for the procedure. The characteristic feature of this part of the book is the weight which the author places on analytical style as illustrated in his frequent paragraphs on "methods of work." The last page is devoted to "Analytical Don'ts," the free translation of one of which well illustrates the author's attitude throughout. "Don't take the time and trouble to separate iron from manganese by a careless application of the quantitative basic acetate method when each may be detected in the presence of the other by a simple color reaction."

The book has many valuable suggestions and for the mineral chemist is well suited to the purpose for which it was written. It is not suitable for a teaching book unless used as a laboratory manual in connection with one of the larger works on Qualitative Analysis. R. S. WILLIAMS

GRUNDRISS DER ANORGANISCHEN CHEMIE. Von PROF. CARL OPPENHEIMER. VII Auflage. Leipzig: Verlag von GEORG THIEME. 1912. pp. 196. Price, M. 3.50.

This book, which is intended for the use of medical students, pharmacists, architects, etc., contains a considerable amount of information in a very condensed form. It may be of use to one who wishes to learn enough to pass an examination, but is of little value to one who wishes to really know something of the science of chemistry. J. E. G.

No. 456. UNITED STATES CIVIL-SERVICE EXAMINATION

CHEMIST

(Qualified in Physical Chemistry)

A vacancy at present exists in the position of chemist, qualified in physical chemistry, in the Bureau of Standards, Department of Commerce, at Washington, D. C. This position requires a high order of scientific training, equivalent to that

required by the leading American universities for a professorship in physical chemistry. The Government seeks a man with a thorough and broad scientific education and several years' experience and he must possess qualifications of a very high order in the theories of physical chemistry and their applications. He must be qualified to act as adviser in all fields where a knowledge of physical chemistry is required, and be capable of initiating and carrying out researches in the field of the Bureau's varied activities. Ability to take a broad view on chemical subjects is essential. The entrance salary for this position is $3,500 a year.

The Government is endeavoring to find the best man available for this work. The method of selection will be similar to that of an educational institution or business organization whose trustees or governing officers desire to fill a professional or technical position. The qualifications and fitness of applicants will be passed upon by a board containing men of recognized eminence in chemistry. Candidates will not be assembled for examination, but will be rated with respect to their education and training, their technical and professional experience and their achievements, as shown by publications and results accomplished.

Persons interested should write to the United States Civil Service Commission, Washington, D. C. Letters of inquiry must be received by the Commission prior to May 15, 1913. Efforts will be made to reach a decision on this appointment by June 1, 1913.

Issued April 19, 1913

VOL. XLIX JUNE, 1913 No. 6

AMERICAN CHEMICAL JOURNAL

[Contributions from the Chemical Laboratory of Harvard College]

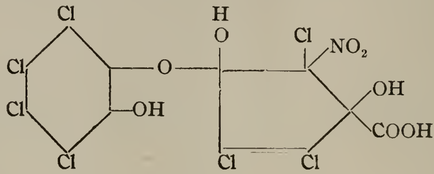
THE ACTION OF NITRIC ACID ON HEPTACHLORPYROCATECHINORTHOQUINO HEMIETHER[1]

BY C. LORING JACKSON AND G. L. KELLEY

The heptachlor hemiether, $C_6Cl_4(OH)OC_6Cl_3O_2$, when warmed with glacial acetic acid and a little fuming nitric acid, is converted into a new compound, $C_{12}H_4O_8NCl_7$, formed by the addition of the elements of a molecule of nitric acid and one of water to the original substance. It melts at temperatures between 176° and 198°, according to the speed with which it is heated, that is, according to the greater or less degree of decomposition it has undergone before the melting point is reached. Cases of this sort have been not uncommon in work on the orthoquinones, where most of the bodies decompose as they melt, but this substance and those related to it show this variation in an extreme form, so that the melting point is of no value in determining the purity of a compound. Accordingly, in order to get some criterion of purity, we purified seven specimens by different methods, and since analyses of these gave maximum differences of 0.78 per cent. on the chlorine and 0.88 per cent. on the carbon, we feel no doubt that our substance is a definite compound, and was pure.

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by George Leslie Kelley.

In trying to determine the structure of this body we have encountered great difficulties—in fact, the publication of this paper has been delayed more than a year on this account, and even now the best graphic formula we have found is open to a serious objection; but, as it explains the other reactions of the compound satisfactorily, and there is much evidence that weakens the force of this objection, we feel justified in accepting this formula (I), according to which the substance is the tetrachlorpyrocatechin hemiether of 2-nitro-2,4,5-trichlor-1,3-dihydroxycyclopentene-1-carboxylic acid,



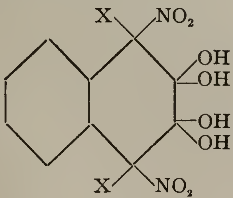
(I)

That this formula explains most of the reactions of the substance is shown by the following discussion of them: Tetrachlorpyrocatechin, $C_6Cl_4(OH)_2$, is easily obtained from it, or several of its derivatives, by the action of hydrochloric acid, sodic methylate, sodic hydroxide,[1] or even boiling water, and this easy breaking of the ether bond would be expected from its neighborhood to one of the hydroxyls.

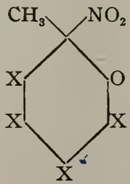
When acted on by acetic anhydride, acetyl chloride, sodic acetate in glacial acetic acid, sodic hydroxide, or even boiling water, an oxide of nitrogen and carbonic dioxide are split off. The removal of carbonic dioxide from cyclopentenehydroxycarboxylic acids by the last two reagents has been observed by Zincke and by Hantzsch, but we have found no cases where it was removed by acetic anhydride or acetyl chloride, which, as a rule, have converted these substances into acetoxy acids. It seems possible, however, that a carboxyl surrounded by so many radicals as in our formula might be

[1] Chloranilic acid appeared sometimes during the action of sodic hydroxide and some other reagents on this compound, but this observation cannot be used in establishing its constitution, since it was proved by a special experiment that chloranilic acid can result from the action of these reagents on tetrachlorpyrocatechin.

decomposed with elimination of carbonic dioxide in the effort of the acetyl group to enter this part of the molecule. The ease with which our compound loses an oxide of nitrogen suggested at first that the nitric acid might be loosely attached, as in a compound of phenanthrenequinone, prepared by Kehrmann and Mattison,[1] or one of fluorenone made by Kurt H. Meyer,[2] but our substance shows no analogy to these, as they are red and decomposed by water quickly and completely, whereas ours is white, and attacked by water only when boiling and then slowly and partially. The easy removal of the oxide of nitrogen, especially by acetic anhydride or acetyl chloride, next seemed to us to point to the presence of a nitrite (—ONO), but the difficulty of obtaining the cycloketone, to be described later, from a nitrite was so great that we have come to the conclusion that our substance contains a nitro group, and its slight stability is not surprising when it is compared with the few analogous ring compounds we have found in the literature, which contain a nitro group attached to the same carbon with another radical. The only bodies we can find, in which this second radical is a halogen, are given by Zincke and Fries[3] (II),



(II)



(III)

and they are decomposed by heatihg with alcohol, glacial acetic acid, or strong sulphuric acid, and are therefore even less stable than our compound, which resists all these reagents. The quinitroles (III) are less closely related to our substance,

[1] Ber. d. chem. Ges., **35**, 343 (1902).

[2] *Ibid.*, **43**, 157 (1910).

[3] Ann. Chem. (Liebig), **334**, 342 (1904). Robertson and Briscoe [J. Chem. Soc., **101**, 1964 (1912)] have prepared a substance probably containing the group $C(NO_2)Cl$ which decomposed with alcohol or chloroform.

but undoubtedly belong to the same class. These lose their nitro groups by the action of benzene even in the cold, of moist cold ether, of acetic anhydride with 10 drops of sulphuric acid,[1] which is especially interesting in this connection, or of boiling glacial acetic acid,[2] so that they also are less stable than our compound.

Although the striking removal of carbonic dioxide and an oxide of nitrogen from our compound was brought about by many different reagents, we succeeded in isolating the organic product only, when acetic anhydride, or acetyl chloride, was used; and this was proved to be an acetyl compound,

$$C_{11}Cl_7O_3C_2H_3O$$

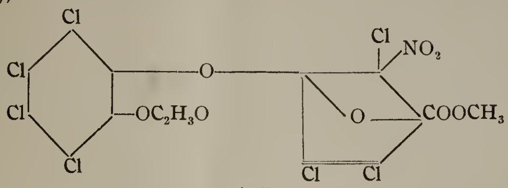
Subtracting from this the acetyl group and the tetrachlorpyrocatechin radical $C_6Cl_4O_2$, there is left C_5Cl_3O, which, according to its properties, can be only a five-carbon ring derived from that given in Formula I. A possible explanation of the mechanism of this reaction will be given later. Of the other reagents which produced this effect, the action of sodic hydroxide and of boiling water was to be expected, but, so far as we can find, the removal of carbonic dioxide and an oxide of nitrogen by sodic acetate dissolved in glacial acetic acid is without analogy, for in the few cases where sodic acetate has been used heretofore in related work it did not decompose the five-carbon ring acid. Possibly this difference in behavior may be due to the fact that our predecessors used it dissolved in water instead of in acetic acid.

When our substance was treated with methyl alcohol and sulphuric acid, a compound $C_{13}H_4O_7NCl_7$ was formed by the replacement of one hydrogen by methyl and the removal of a molecule of water; and this body gave a monoacetyl derivative with acetic anhydride, showing that the original substance contains 4 hydroxyls—one converted into methoxyl, two which lose water, and one converted into acetoxyl. This agrees with Formula I; and the acetyl compound is therefore the acetoxytetrachlorpyrocatechin hemiether of 2-nitro-

[1] Zincke, Breitwieser: Ber. d. chem. Ges., **44**, 176 (1911). Zincke: Ann. Chem. (Liebig), **394**, 1 (1912).

[2] Auwers: *Ibid.*, **302**, 163 (1898).

2,4,5-trichlorcyclopentene-1,3-oxide-1-carboxylic methyl ester (IV),



(IV)

It was observed that when a solution of sodic hydroxide was mixed with this ester, the oxide of nitrogen was removed only occasionally, the alkali not acting, as a rule, whereas the removal of the oxide of nitrogen from the free acid took place invariably. This observation is in harmony with our formulas, since nitric acid should be split off from (I) with great ease, but the nitrogen would be detached from (IV) only by a deep-seated reaction. The removal of water by the sulphuric acid and methyl alcohol in forming the ester is surprising in view of the fact that the free acid, after being heated to 100° with strong sulphuric acid alone for a whole day, was recovered unaltered on the addition of water. It should be observed that the want of agreement here is in the experimental results, and while we have found two possible explanations for it based on our formulas, they seem to us not sufficiently probable to be worth recording.

The chlorine in the original substance is firmly attached to the molecule, no hydrochloric acid being removed by sodic hydroxide or any of the other reagents already mentioned. When it is heated to fusion, however, our compound loses, in addition to carbonic dioxide and an oxide of nitrogen, one molecule of hydrochloric acid, which is in accordance with Formula I, but has caused the rejection of most of the other formulas which we have constructed.

While our formula (I), as has been shown, explains most of the reactions already given, there is one serious objection to it. It represents a strong acid, and although our substance, when in alcoholic solution, gives an acid reaction with litmus,

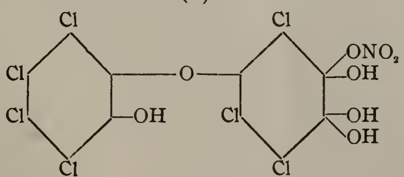
and dissolves in sodic hydroxide, and even sets free a little carbonic dioxide from acid sodic carbonate, it does not act on sodic, calcic, or baric carbonate in cold water. When boiled with baric carbonate and water, it seemed as if more carbonic dioxide was given off than when the substance alone was decomposed by boiling with water, but no barium went into solution. A possible explanation of this behavior with baric carbonate is that the substance was too slightly soluble in cold water to act upon it, and that, when hot, the barium salt was formed, but was immediately broken up by the boiling water with the formation of baric carbonate, a behavior in harmony with our knowledge of such salts. While this explains the action with baric carbonate fairly well, it does not show why the soluble sodic carbonate should be unaffected, when action is obtained on the one hand with sodic hydroxide and on the other with acid sodic carbonate. It must be confessed, therefore, that our substance behaves more like an acid phenol than like a carboxylic acid. We have tried to meet this serious objection to our formula (I) in two ways; (*A*) by bringing forward other properties of our substance, which point to the presence of a carboxyl group in it, and (*B*) by showing that other formulas are open to even greater objections.

A. Although most of the five-carbon ring hydroxy acids seem to give salts with ease, Zincke and Küster[1] have described two from which they were obtained with great difficulty; in fact, only the barium salt could be made, and this by the action of baric hydroxide on an alcoholic solution. No mention is made of experiments with carbonates, but this fact, coupled with the unusual way of preparing the barium salt, makes it seem probable that these two undoubted carboxyl acids behaved toward them abnormally, possibly like ours. The formation of our ester by the action of alcohol and sulphuric acid indicates the presence of a carboxyl acid, but it cannot be accepted as a proof, since there are many cases on record in which a phenol hydroxyl with negative environment is con-

[1] Ber. d. chem. Ges., **21**, 2719 (1888); **23**, 812 (1890).

verted into an alkoxyl under these conditions.[1] Hoffmann[2] gave as a proof of the presence of carboxyl in these cyclohydroxycarboxyl acids the fact that their esters were saponified by aqueous sodic hydroxide *in the cold*, since Salkowski[3] had found that even picryl ether must be boiled with alkali for a long time before it is decomposed. In applying this proof to our methyl compound no decisive result was obtained. It dissolved partially in cold sodic hydroxide, but the solution was not complete until it had been boiled, when a far-reaching decomposition took place. The fact that it dissolved at all, however, seems to us to point strongly to the presence of carboxyl. When our compound was heated to 100° with phosphoric pentachloride and oxychloride, hydrochloric acid was given off in large quantity, and after treatment with water to destroy the chlorides of phosphorus the unaltered substance was recovered. This certainly is most easily explained by the formation of an acid chloride converted again to the acid by water, whereas, if the acidity is caused by a phenol hydroxyl instead of a carboxyl, the original substance would not have been obtained. While no one of these observations gives an absolute proof of the existence of carboxyl in our substance, together they furnish a considerable body of evidence in favor of it.

B. If the acid properties are due to a phenol hydroxyl and not to a carboxyl, we can find no way of representing the substance except with two six-carbon rings; and the best formula of this sort we have found is (V).

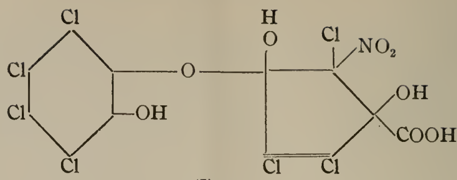


(V)

[1] For instance, Ber. d. chem. Ges., **17,** 2106 (1884); **21,** 603, 1900 (1888). Monats. Chem., **21,** 875 (1900). Ber. d. chem. Ges., **38,** 2864 (1905); **15,** 1427 (1882). Ann. Chem. (Liebig), **244,** 72 (1887). J. Chem. Soc., **77,** 3344 (1900). D. R. P., 173,730 (1906).

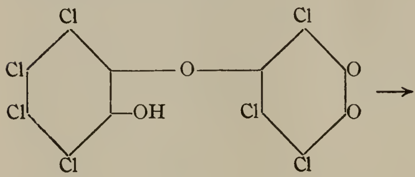
[2] Ber. d. chem. Ges., **22,** 1263 (1901).

[3] Ann. Chem. (Liebig), **174,** 259.

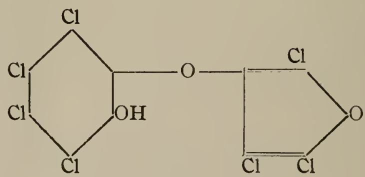


(I)

The most striking reaction studied by us was the conversion of the quino hemiether (VI) into the cycloketone (VII) by the action of nitric acid:



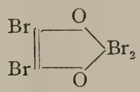
(VI)



(VII)

(giving the intermediate product I or V), followed by that of acetic anhydride. The formation of the cycloketone (VII) must be preceded by the formation of a five-carbon ring acid like (I), and the question arises, in what stage of the process is this acid formed? If by the nitric acid, (I) is the formula of the intermediate product; if by the acetic anhydride, (V) or some other similar formula represents the structure of this compound. When it is remembered that the conversion of the six-carbon into the five-carbon ring acid consists in adding water to the former, it is hardly conceivable that this change can have been brought about by acetic anhydride, in which

case no water can be obtained from outside, and although the molecule of (V) contains exactly the necessary amount of water, there seems no chance that it would take part in this reaction before it was removed by the acetic anhydride, which must convert $C(OH)_2$ into CO. This seems to us a conclusive argument against (V) and all other six-carbon ring formulas. On the other hand, the formation of (I) from (VI) by nitric acid is not without analogy, for, although such acids have usually been formed by the action of alkalies, Flint and one of us[1] obtained the compound



(VIII)

by the action of nitric acid and bromine on tetrabromorthoquinone, which must have been preceded by the formation of a five-carbon ring hydroxycarboxylic acid.[2]

Although the argument given above seems to us to disprove all six-carbon ring formulas, we add, by way of confirmation, a few properties of our substance, which agree with the view that it contains a five- rather than a six-carbon ring. Its very marked stability toward acids, and the ease with which alkalies act on it, recall at once the five-carbon cycloketone (VIII) of Flint and one of us, since these were among its most striking properties, and a similar stability toward acids has been observed by Hantzsch.[3] He has also obtained several six-carbon rings more or less modified by additions analogous to (V) and related formulas,[4] but they are easily converted again to the original aromatic or quino compound by a number of reactions, including reduction. Our substance is reduced only with a great deal of difficulty, and in no case have we observed a return to the quino body. This is the more striking

[1] This Journal, **43**, 135 (1910).

[2] Compare also Zincke and Gerland [Ber. d. chem. Ges., **20**, 3216 (1887)] and Zincke and Küster [*Ibid.*, **21**, 2917 (1888); **23**, 812 (1890)] who obtained such acids by the action of boiling water.

[3] Ber. d. chem. Ges., **20**, 2780 (1887); **22**, 1238 (1889).

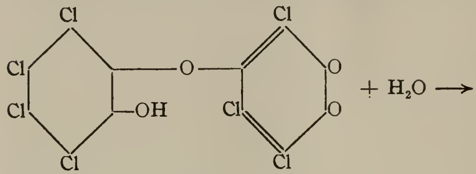
[4] Hantzsch: *Ibid.*, **21**, 2421 (1888).

because the red hexachlororthoquinopyrocatechin ether,

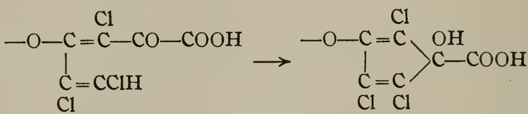
$$C_6Cl_4O_2C_6Cl_2O_2$$

has appeared with great frequency in our experiments with tetrachlororthoquinone and its derivatives. Its complete absence throughout our work with this substance can therefore be taken as evidence that the quino ring here undergoes a deep-seated transformation.

The formation of our substance from the hemiether (VI) is represented by the following sequence of formulas:

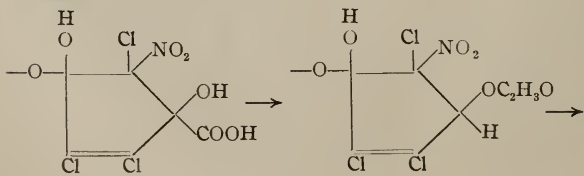


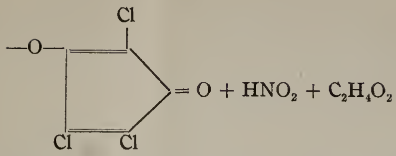
(VI)



followed, or preceded, by the addition of nitric acid to the upper double bond to give (I).

The mechanism of the reaction by which acetic anhydride converts the acid (I) to the cycloketone (IX) may perhaps be explained as follows: The acetic anhydride, in trying to force its way against the steric hindrances to the hydroxyl which is surrounded by so many radicals, drives out carbonic dioxide from the carboxyl:

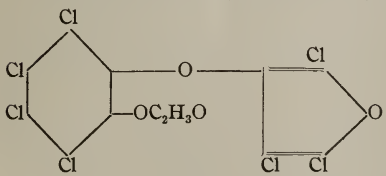




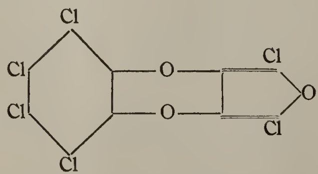
and the acetate of a secondary alcohol thus formed has such a tendency to be oxidized that it removes the nitric acid from the ring, and is converted by it into the ketone and acetic acid; or this last step may consist of a substitution followed by oxidation, as follows:

$$2 >CHOC_2H_3O + 2HNO_3 \longrightarrow$$
$$2 >CH(ONO_2) + 2C_2H_4O_2 \longrightarrow$$
$$2 >CO + N_2O_3 + H_2O$$

The formula of the cycloketone is (IX), and it is therefore



(IX)



(X)

the acetoxytetrachlorpyrocatechin hemiether of trichlor-ketocyclopentadiene.

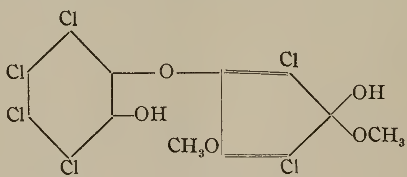
The acetyl group can be replaced by hydrogen by treatment with hydrochloric acid and alcohol. The original acetyl compound, or its hydroxyl derivative, if treated with pyridine, is converted into a vivid red compound (Formula X), therefore, the tetrachlorpyrocatechin ether of dichlorketocyclo-

pentadiene. That pyridine could remove acetyl chloride under such circumstances was shown by an experiment, in which it converted the acetyl hemiether,

$$C_6Cl_4(OC_2H_3O)OC_6Cl_3O_2$$

into the complete ether, $C_6Cl_4O_2C_6Cl_2O_2$. We found, however, to our surprise, that we could not get the complete ether from the benzoyl compound $C_6Cl_4(OC_7H_5O) — O — C_5Cl_3O$, by the action of pyridine.

The two complete ethers, (X) and $C_6Cl_4O_2C_6Cl_2O_2$, resemble each other very closely, which is a strong argument in favor of our formula. Thus, they are both vivid red,[1] whereas the corresponding hemiethers are but slightly colored; the melting points are very high; and they are very slightly soluble. Formula X is also supported by the fact that, when treated with sodic methylate in methyl alcohol, our ether-ketone takes up two molecules of methyl alcohol, forming, after acidification, the tetrachlorpyrocatechin hemiether of -hydroxy-1,4-dimethoxy-2,5-dichlorcyclopentadiene (XI), which is to be ex-



(XI)

pected, as our previous work has shown that hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O_2$, takes up alcohols easily, forming alkoxyl hemiethers.

The fact that we did not succeed in preparing an oxime from this substance (X), or any of those related to it, does not tell against our formula, since a ketone containing so much chlorine would form an oxime with difficulty, if at all. When heated to 225°–240°, our red compound (X) turns white,

[1] This strong color may be connected with the symmetrical structure of these ethers, but further experiment is necessary before this explanation can be accepted.

and this change of color is accompanied by a loss of about 18 units of molecular weight. All our attempts to explain this behavior are mere guess work with our present knowledge, since the organic product was so unmanageable that we were unable to obtain any information about it with the amount at our disposal, because at the time we made this observation we could no longer prepare the red ether, although it had been obtained with ease in our earlier work. For this reason we have been obliged to leave our work on this compound in a decidedly unfinished state in other respects also.

By the action of nitric acid and glacial acetic acid on the hexachlormethoxyorthoquinopyrocatechin hemiether,

$$C_6Cl_4(OH)OC_6Cl_2(OCH_3)O_2$$

a substance was obtained which analyzed for

$$C_6Cl_4(OH)OC_5Cl_2(OCH_3)(NO_2)(OH)_2COOH$$

but it is doubtful whether it is related to the tetrachlorpyrocatechin hemiether of 2-nitro-2,4,5-trichlor-1,3-dihydroxycyclopentene-1-carboxylic acid (I), because with acetic anhydride it forms a monoacetyl compound, instead of undergoing the far-reaching decomposition to a cycloketone like this substance. The determination of its structure must be left for future work. Several compounds have been obtained in the course of this work which we could not study thoroughly. Provisional structural formulas for them in harmony with those already discussed will be found in the experimental part.

EXPERIMENTAL

Action of Nitric Acid on Heptachlororthobenzoquinopyrocatechin Hemiether

Twenty grams of the hemiether, $C_6Cl_4(OH)OC_6Cl_3O_2$, dissolved by the aid of gentle heat in enough glacial acetic acid to form a solution saturated at ordinary temperatures, were mixed with 5 cc. of fuming nitric acid (specific gravity 1.5), and, after the mixture had been warmed for 5 minutes to a temperature not above 65°, water was added to the warm solution until a slight permanent cloudiness had been formed, when on cooling a mass of crystals separated, or more commonly a red oil was deposited, which was converted into crys-

tals by stirring with a glass rod in contact with water; or, if it remained obstinately liquid, the crystals could usually be obtained by washing with successive portions of water followed by scratching with the glass rod. On diluting the mother liquor an additional fairly large amount of crystals was obtained. Earlier in our work the whole of the product was thrown down by an excess of water, but the subsequent purification was much more difficult in this case than in that just described, which was the result of a careful study of the conditions of the reaction. Even with the utmost care, however, the process failed occasionally.

The crystals obtained as described above were usually red, but most of the color was removed on washing by decantation with large quantities of water, after which they were collected, dried on a steam plate, powdered, and boiled with a mixture of 3 parts of benzene to one of ligroin, which dissolved out a troublesome viscous impurity without taking up much of the substance. The residue, freed from ligroin by drying, was dissolved in hot benzene, and precipitated by ligroin, when ill-defined crystals were obtained. In about 5 out of 30 or 40 preparations a product melting with decomposition between 159° and 165° was obtained, while in the remainder the product melted between 176° and 198°. In both cases the variation in the decomposition point caused by different conditions of heating was unusually large, so that this point was essentially of no value in determining the purity of the substance.

Compound Melting between 159° and 165°; Perhaps the Tetrachlorpyrocatechin Hemiether of the Nitrodichlorhydroxycyclopentadienecarboxylic Acid, $C_{12}H_3O_7NCl_6$.—We have not found the conditions on which the formation of this compound depended, and therefore obtained it only by accident, but, as it appeared chiefly in the earlier parts of the work, we should study the effect of slightly smaller amounts of nitric acid and precipitation of all the organic matter at once by water, if it were important enough to make it worth while to find out the conditions for its formation. It was purified by repeated crystallization from a mixture of benzene and

ligroin, and two different samples (I–IV and V–VI) were analyzed in the hope of proving it was a definite compound, as the decomposition point could not be used for this purpose.

I. 0.2747 gram substance, dried at 130°, gave 0.3090 gram CO_2 and 0.0440 gram H_2O.

II. 0.3945 gram substance gave 0.4409 gram CO_2 and 0.0546 gram H_2O.

III. 0.6285 gram substance gave 13.20 cc. moist N_2 at 15°.6 and 765 mm.

IV. 0.1166 gram substance gave 0.2094 gram AgCl.

V. 0.1087 gram substance dried at 80° gave 0.1962 gram AgCl.

VI. 0.1092 gram substance gave 0.1981 gram AgCl.

	Calculated for $C_{12}H_3O_7NCl_6$	Found I	II	III	IV	V	VI
C	29.63	30.68	30.48	...	...	...	...
H	0.62	1.78	1.54	...	...	...	...
N	2.88	...	...	2.47	...	...	...
Cl	43.85	...	...	...	44.38	44.62	44.85

The formula $C_6Cl_4(OH)—O—C_5Cl_2(OH)(NO_2)COOH$ may be provisionally assigned to this substance.

Properties of the Tetrachlorpyrocatechin Hemiether of the Nitrodichlorhydroxycyclopentadienecarboxylic Acid (?)—From alcohol and water, white or cream-colored flosslike crystals are obtained, while from benzene and ligroin crystals of rather an indefinite form are deposited. It melts with effervescence as low as 159°, if heated slowly, but by rapid heating it can be made to melt as high as 165°. It is soluble in all the common solvents, even in hot water, from which it is deposited in flocks; but it does not crystallize well from any of its solutions, the best solvent for it being a mixture of benzene and ligroin. The strong acids have no apparent action on it, but it is soluble in sodic or ammonic hydroxide with a pale yellow color. Owing to the small amount of material at our disposal, all these results must be considered preliminary.

Compound Melting between 176° and 198°. Tetrachlorpyrocatechin Hemiether of 2-Nitro-2,4,5-trichlor-1,3-dihydroxycyclopen-

tene-1-carboxylic Acid, $C_6Cl_4(OH)—O—C_5Cl_3(OH)_2(NO_2)COOH$. —In purifying this substance, which was the usual product of the reaction, we found differences of as much as 32° between the decomposition points of specimens purified in different ways. As these differences are to be ascribed in great part to the unusually strong influence of different conditions on the decomposition point, this property cannot be used as a criterion of purity. To take its place we have analyzed specimens purified in a number of different ways (*A–G*) with the results given below:

A. Purified by crystallization from benzene and ligroin followed by glacial acetic acid and water.

B. Crystallized from benzene and ligroin followed by methyl alcohol.

C. Crystallized from benzene and ligroin.

D. *C* recrystallized once from methyl alcohol and once from benzene and ligroin.

E. Crystallized once from each of the following solvents: benzene and ligroin, ethyl alcohol and water, methyl alcohol and water, benzene and ligroin.

F. Crystallized twice from each of the following solvents: benzene and ligroin, methyl alcohol, acetone, and finally once from benzene and ligroin.

G. Crystallized several times from gla ial acetic acid and water.

	Melting point	Analyses
A	160°	Cl 46.00
B	176°	Cl 45.33, 45.62
C	181°–182°	Cl 45.82, 46.00; C 26.59; H 1.89
D	192°	Cl 45.66, 45.74; C 27.46; H 1.60
E	...	C 27.31, 27.01; H 1.21, 1.86; N 2.87
F	188°	Cl 45.96, 46.08
G	180°	Cl 46.11

The maximum differences between the determinations are 0.78 for chlorine and 0.88 for carbon, and therefore it is safe to infer that the substance is a definite compound, and pure or nearly so in all the cases. As the details of some of these analyses should be given, we have selected *E* (I–III)

and *F* (IV–V) as the most thoroughly purified specimens. They were dried at 94°.

I. 0.4746 gram substance gave 0.4752 gram CO_2 and 0.0517 gram H_2O.

II. 0.2644 gram substance gave 0.2618 gram CO_2 and 0.0441 gram H_2O.

III. 0.3113 gram substance gave 8.01 cc. moist N_2 at 22°.3 and 757 mm.

IV. 0.1297 gram substance gave 0.2411 gram AgCl.

V. 0.1165 gram substance gave 0.2171 gram AgCl.

	Calculated for $C_{12}H_4O_8NCl_7$	Found I	II	III	IV	V
C	26.74	27.31	27.01	....	...	...
H	0.74	1.21	1.86	....	...	...
N	2.59	...	...	2.87	...	...
Cl	46.15	...	...	....	45.96	46.08

Molecular-weight determinations by the boiling-point method:

VI. 0.6348 gram substance in 19.07 grams benzene, Δ = 0°.162, K = 26.70.

VII. 0.643 gram substance in 18.52 grams acetone,[1] Δ = 0°.117.

VIII. 3.109 grams substance in 17.28 grams acetone, Δ = 0°.600.

	Calculated for $C_{12}H_4O_8NCl_7$	Found VI	VII	VIII
Mol. wt.	538.5	549	512	517

These results indicate that the substance was formed by the addition of the elements of one molecule of nitric acid and one of water to the heptachlor hemiether, $C_6Cl_4(OH)OC_6Cl_3O_2$, and for reasons given in the introduction we have assigned to it provisionally the constitution represented by the following name:

Properties of the Tetrachlorpyrocatechin Hemiether of 2-Nitro-2,4,5-trichlor-1,3-dihydroxycyclopentene-1-carboxylic Acid.—The best formed crystals are obtained from methyl alcohol, and have a hexagonal shape with modifications, which could not

[1] K = 17.25. Jones: This Journal, **31**, 114 (1899).

be identified on account of their small size, but there was always deposited from this solvent a viscous ring on the side of the dish even after many recrystallizations. From ethyl alcohol and water needles are obtained; from the other common solvents it is deposited in indefinite flakes, or as a viscous mass. The purest specimens were nearly white with a brownish tinge. It melts with effervescence at temperatures which are much influenced by the conditions of heating; the highest point obtained was 198° by dipping the tube into the hot bath, but by slow heating the same specimen could be made to melt at 176°. The gases given off during the melting contained carbonic dioxide, an oxide of nitrogen, hydrochloric acid, and water recognized by the usual tests. The loss in weight, when heated till constant between 195° and 200°, was studied quantitatively; six determinations gave the following percentages: 26.14, 26.02, 25.1, 24.3, 27.7, 26.72. The residues from the last two determinations contained 53.50 and 53.84 per cent. of chlorine; a loss of one molecule each of carbonic dioxide, hydrochloric acid, water and nitric dioxide would amount to 26.81 per cent., and a new substance formed by such a loss would contain 53.93 per cent. of chlorine. The residue was so unmanageable that we were unable to isolate any definite substance from it.

The nitro hemiether is freely soluble in alcohol, ether, acetone, or glacial acetic acid; moderately soluble in chloroform, tetrachloride of carbon, or benzene; nearly insoluble in ligroin or water.

When boiled with water it is slowly decomposed, yielding carbonic dioxide, recognized by the precipitate with baryta water; an oxide of nitrogen, detected by its action on diphenylamine dissolved in strong sulphuric acid; and tetrachlorpyrocatechin, recognized by its melting point, 194–195°, solubilities and reactions with ferric chloride and with nitric acid; there was also a considerable amount of tar, from which we could extract nothing further.

This decomposition by boiling water seems to be prevented by the presence of acetic acid, or hydrochloric acid. The substance is, in fact, remarkably stable toward acids, as speci-

mens heated on the steam bath for a whole day with sulphuric acid were recovered unaltered on dilution. Strong nitric acid, or hydrochloric acid, is without apparent action on it in the cold.

A solution of the substance in alcohol and water reddens litmus paper, and, if the powdered solid is dropped into a cold solution of acid sodic carbonate, there is a slight effervescence, but none could be obtained from neutral sodic carbonate or from calcic or baric carbonates in the cold. As already stated, it gives off carbonic dioxide, when boiled with water alone; but, if baric carbonate was also present, the evolution of gas seemed to be somewhat greater, and in one case clusters of white plates melting at 190° were obtained, but in too small quantity for study. No barium, however, could be detected in the solution. Cold sodic hydroxide dissolves it, but it is not reprecipitated by acids. On standing, the solution develops the characteristic purple color of chloranilic acid. On warming a solution of the substance in aqueous sodic hydroxide, fine black particles appeared in the liquid, which were filtered off, and yielded no definite compound. The filtrate, after acidification, gave a blue color with diphenylamine, and green with ferric chloride, so probably some oxide of nitrogen and some chlorpyrocatechin had been formed, but the ether extract from it, when evaporated to dryness on the steam bath, gave a viscous residue, which took fire spontaneously the first but not the second time we obtained it. Attempts were made to prepare the lead salt from a solution of the substance in acetone or methyl alcohol by adding sodic hydroxide till faintly alkaline, then a drop of acetic acid and plumbic acetate until a precipitate ceased to form (a special experiment had shown that a larger quantity of water than that contained in the plumbic acetate gave no precipitate with our solution). The precipitate was washed with acetone (or methyl alcohol) and water, and dried for analysis. Five specimens gave percentages of lead varying from 30.45 to 45.52 ($C_{12}H_2O_8NCl_7Pb$, Pb_2 7.84) so that it was evident we had not prepared a definite compound. This lead salt, treated with ethyl iodide either alone or with alcohol, benzene, or glacial

acetic acid, gave much plumbic iodide, but no organic substance could be isolated from the product.

A two per cent. solution of sodic methylate in methyl alcohol dissolved the substance in the cold, and the solution became straw-colored after a few minutes. On dilution with acidified water a precipitate was formed, which was identified as tetrachlorpyrocatechin, while the filtrate showed the characteristic color of chloranilic acid, and gave a test for an oxide of nitrogen with diphenylamine. Viscous substances were also observed, one yellow and soluble in benzene, the other red and insoluble, but they were so unpromising that they were not studied. Sodic ethylate seemed to cause a less extensive decomposition, but the products were no more satisfactory.

Pyridine produced no visible change in the cold with a solution of the compound in alcohol, or glacial acetic acid, but on warming the liquid turned dark, and a gas was given off. On adding water a pink or brown precipitate was thrown down, from which no crystals could be isolated. We have some reason to think that a better result might be obtained by carefully regulating the length of the heating. Phenylhydrazine, benzylphenylhydrazine, aniline and dimethylaniline gave an evolution of gas and similar black solutions in which no definite organic products could be found.

When a mixture of sodic acetate, glacial acetic acid and the substance was heated on the steam bath, carbonic dioxide and oxides of nitrogen were given off, whereas no such decomposition took place with glacial acetic acid alone. The solution contained much chloranilic acid, and a pale yellow substance crystallizing from methyl alcohol in long prisms melting after one crystallization at 170°, while there was suspended in it a white substance insoluble in the ordinary solvents, which blackened at 260°. Both these substances appeared in such small quantities that we did not attempt to investigate them. Argentic acetate, heated with a solution of our compound in glacial acetic acid, or methyl alcohol, gave two white products, one freely soluble in alcohol but insoluble in benzene, which melted at 180° after two crystallizations, but still contained traces

of silver; the other less soluble in alcohol, from which it could be obtained in needles, was free from silver and nitrogen. In practice the experiments did not seem so promising as in this account of them, and therefore were not continued.

The substance was moistened with phosphoric oxychloride covered with twice its weight of phosphoric pentachloride, and heated under a return condenser on the steam bath for three hours, when it liquefied, and gave off hydrochloric acid in quantity, but on pouring the cooled solution into water the unchanged substance was recovered, as it gave the characteristic hexagonal crystals from methyl alcohol and contained 45.78 per cent. of chlorine instead of the 46.15 per cent. required by the theory; melting point, 186°–188°. In another experiment phosphoric pentachloride alone was used, and the mixture was heated to 110°. In this case we did not succeed in freeing the unmanageable viscous product from phosphorus. Exactly the result which would be expected, if the hydroxyl had taken part in the reaction.

The substituted pyrocatechin cyclopentenehemiethercarboxylic acid offers a marked resistance to reducing agents; no action was observed with sulphurous dioxide with water, alcohol, or glacial acetic acid, or with zinc and hydrochloric acid; tin and hydrochloric acid turned the solid yellow, but the action was a superficial one, as most of the substance proved to be unchanged. Accordingly, the body was treated with glacial acetic acid mixed with an equal volume of strong hydrochloric acid and heated with tin on the steam bath. After an hour the solid had gone into solution, and the product was then precipitated with water acidified with hydrochloric acid. The white, viscous precipitate could not be made to crystallize, and after many efforts to purify it by precipitation the work was abandoned, as the results promised not to be worth the amount of time necessary to obtain them. The action of acetic anhydride, of acetyl chloride or of benzoyl chloride is described later.

Tetrachlorpyrocatechin Hemiether of 2-Nitro-2,4,5-trichlor-1,3-dihydroxycyclopentene-1-carboxylic Methyl Ester, $C_6Cl_4(OH)OC_5Cl_3(OH)_2(NO_2)COOCH_3$.—One gram of the acid

was dissolved in the least quantity of acetone and treated with a 1 : 5 solution of sodic hydroxide till strongly alkaline, when 5 cc. of dimethyl sulphate were added gradually with shaking and cooling. Afterward more of the sodic hydroxide was added, continuing the shaking and cooling until a precipitate appeared and the mixture had become permanently alkaline. After standing for half an hour, it was precipitated with water and enough hydrochloric acid to acidify it, and the precipitate was washed with water, dried, and recrystallized at first from alcohol and water, later from acetone containing a little ligroin, till it melted at 221°, when it was dried at 130°.

I. 0.1073 gram substance gave 0.1967 gram AgCl.

II. 0.1002 gram substance gave 0.1821 gram AgCl.

	Calculated for $C_{13}H_6O_8NCl_7$	Found I	Found II
Cl	44.97	45.34	44.94

There was not enough of the substance for a combustion, and our later attempts to prepare it gave a different product, in which we succeeded in recognizing tetrachlorpyrocatechin by its crystalline form, solubilities, melting point, 194°–195°, and color with ferric chloride, and tetrachlorveratrol, detected by the melting point, 89°–90° instead of 88°, according to Brüggemann,[1] by its crystalline form, solubilities and volatility with steam, and confirmed by an analysis of a somewhat impure specimen, which gave results as near as could be expected. These later results were evidently due to the decomposition of the hemiether by the sodic hydroxide.

Properties of the Methyl Ester Melting at 221°.—It does not crystallize well from any common solvent, but the best result was given by acetone with a little ligroin, from which it was deposited in clusters of rather indefinite cream-white needles. It melts with effervescence at 221°, the gases formed giving a blue color with diphenylamine. It is soluble in all the common organic solvents except ligroin. Acids and alkalies produce no apparent change; occasionally the alkaline solutions gave a blue color with diphenylamine, but more commonly no reaction could be obtained.

[1] J. prakt. Chem., [2] **53**, 251.

Action of Sulphuric Acid and Methyl Alcohol on the Nitrohemiether

Tetrachlorpyrocatechin Hemiether of the 2-Nitro-2,4,5-trichlorcyclopentene-1,3-oxidecarboxylic Methyl Ester, $C_6Cl_4(OH)OC_5Cl_3O(NO_2)COOCH_3$.—This reaction was tried in the hope of finding an easier method for the preparation of the methyl ether just described, but, although a methyl group was introduced, a molecule of water was removed at the same time, giving the substance mentioned in the title. One part of the nitro hemiether was dissolved in 10 parts of methyl alcohol, and 20 of strong sulphuric acid were added slowly, when much heat was evolved. The mixture was then heated on the steam bath from 4 to 6 hours. During this time white crystalline flakes appeared, the quantity of which increased when the mixture was allowed to stand overnight. The solution was poured off, the crystals washed thoroughly with small portions of methyl alcohol, in which they are only slightly soluble, and then crystallized, at first from a mixture of benzene and ligroin, afterward from tetrachloride of carbon and ligroin, and dried for analysis.

I. 0.2501 gram substance gave 0.2675 gram CO_2 and 0.0259 gram H_2O.

II. 0.2172 gram substance gave 0.2308 gram CO_2 and 0.0228 gram H_2O.

III. 0.1076 gram substance gave 0.2020 gram AgCl.

IV. 0.1039 gram gave 0.1950 gram AgCl.

	Calculated for $C_{13}H_4O_7NCl_7$	Found I	II	III	IV
C	29.18	29.17	28.98	...	...
H	0.75	1.16	1.17	...	...
Cl	46.49	...	...	46.42	46.39

Properties of the Tetrachlorpyrocatechin Hemiether of the 2-Nitro-2,4,5-trichlorcyclopentene-1,3-oxidecarboxylic Methyl Ester.—It crystallizes from tetrachloride of carbon in compact clusters of needles, from most of the other organic solvents in thin rhombic plates. It melts at temperatures between 221° and 228°, according to the speed of the heating, forming a colorless liquid and giving off gases which produce a blue

color with diphenylamine in strong sulphuric acid. It is easily soluble in benzene, chloroform, or tetrachloride of carbon; slightly soluble in alcohol, or ligroin. These solubilities, combined with its tendency to crystallize, make it easy to purify, in pleasing contrast to most of the related substances. The three strong acids are without apparent action on it. It dissolves slightly in a cold solution of an alkali, completely if warmed, giving an orange solution, which turns red on acidification, possibly from a trace of chloranilic acid, and deposits tetrachlorpyrocatechin, but these reactions do not appear always by any means. This alkaline solution gave a blue test with diphenylamine also only occasionally. Sodic methylate gave an unpromising viscous product.

Acetyl Derivative of the Methyl Ester, $C_6Cl_4(OC_2H_3O)OC_5Cl_3O(NO_2)COOCH_3$.—Five grams of the substance melting at 221°–228° described above were heated with twenty grams of acetyl chloride for two hours on the steam bath under a return condenser, the liquid was then evaporated off, the white residue washed with methyl alcohol, and purified by adding hot methyl alcohol to a hot benzene solution of the compound, when some crystals were precipitated at once, and the amount was increased as the liquid cooled. It melted at 189° and was dried at 120°.

I. 0.5639 gram substance gave 0.6538 gram CO_2.

II. 0.4155 gram substance gave 0.4813 gram CO_2 and 0.0467 gram H_2O.

III. 0.1515 gram substance gave 0.2637 gram AgCl.

IV. 0.1713 gram substance gave 0.3010 gram AgCl.

V. 0.7590 gram substance gave 20.08 cc. moist N_2 at 28° and 764.8 mm.

	Calculated for $C_{15}H_6O_8NCl_7$	Found I	II	III	IV	V
C	31.23	31.62	31.59	...	...	....
H	1.04	...	1.26	...	...	....
Cl	43.11	...	...	43.04	43.00	....
N	2.43	...	...	...	...	2.92

I. 0.5995 gram substance in 26.17 grams C_6H_6 gave Δ 0°.226.

II. 1.0999 grams substance in 26.17 grams C_6H_6 gave Δ 0°.418 by the freezing-point method; $K = 51.00$.

	Calculated for $C_{15}H_6O_8NCl_7$	Found I	II
Mol. wt.	576.5	517	513

Occasionally a substance melting at 224° was obtained instead of that analyzed, but we could not prepare enough of this for analysis; in one case the acetyl chloride left the substance unaltered.

Properties of Tetrachlorpyrocatechinacet Hemiether of 2-Nitro-2,4,5-trichlorcyclopentene-1,3-oxidecarboxylic Methyl Ester.—It crystallizes from benzene and alcohol in white rhombic prisms, which melt at 189° with effervescence to a straw-colored liquid. Easily soluble in benzene; slightly soluble in alcohol, ether, tetrachloride of carbon, glacial acetic acid, or ligroin; insoluble in water. Strong acids, or alkalies, produce no visible effect on it in the cold. The hydrochloride of hydroxylamine did not act on the substance, when heated with it in alcoholic solution. When the experiment was tried in presence of somewhat less than the calculated amount of sodic carbonate, the acetyl group was removed, leaving the methyl ether, shown by the melting point 226°–228°, and an analysis for chlorine which gave 46.09 per cent. instead of 46.49.

Tetrachlorpyrocatechinacet Hemiether of Trichlorketocyclopentadiene, $C_6Cl_4(OC_2H_3O)OC_5Cl_3O$.—Five grams of the nitro hemiether melting at 176°–198° were heated in an Erlenmeyer flask with 10 cc. of acetic anhydride on the steam bath for half an hour, when it was found that carbonic dioxide and an oxide of nitrogen were given off, the former recognized by its action with baric hydroxide, the latter by the appearance of a blue color in a solution of diphenylamine in sulphuric acid. The liquid was allowed to evaporate spontaneously, and the viscous residue was dissolved in its own volume of benzene, and upon dilution with three or four times its volume of alcohol deposited white scales. These, after washing with alcohol, were crystallized from a mixture of benzene and alcohol, until they showed the constant melting point 165°, when they were dried at 100° for analysis. Although the compound was only slightly soluble in alcohol, it was a difficult matter to free it from its viscous impurity. Acetyl chloride gave the same

results, but in this case the warming should take place under a return condenser.

I. 0.3166 gram substance gave 0.3840 gram CO_2 and 0.0271 gram H_2O.

II. 0.3632 gram substance gave 0.4427 gram CO_2 and 0.0278 gram H_2O.

III. 0.1744 gram substance gave 0.3699 gram AgCl.

IV. 0.1478 gram substance gave 0.3151 gram AgCl.

V. 0.1490 gram substance gave 0.3149 gram AgCl.

	Calculated for $C_{13}H_3O_4Cl_7$	Found I	II	III	IV	V
C	33.09	33.08	33.24	...	...	...
H	0.64	0.96	0.85	...	...	...
Cl	52.70	...	...	52.44	52.71	52.25

III, IV and V were analyses of specimens from three different preparations, and these results were confirmed by another combustion and two other chlorine determinations.

I. 0.5290 gram substance in 21.20 grams C_6H_6 gave Δ 0°.275.

II. 0.9495 gram substance in 21.20 grams C_6H_6 gave Δ 0°.510 by the freezing-point method.

	Calculated for $C_{13}H_3O_4Cl_7$	Found I	II
Mol. wt.	471.5	463	447

Properties of the Tetrachlorpyrocatechinacet Hemiether of Trichlorketocyclopentadiene.—It crystallizes from a mixture of benzene and alcohol in white glistening rhombic plates, which melt at 165°, although under special conditions a temperature as high as 168° was observed. Soluble in most of the common organic solvents; slightly soluble in ethyl or methyl alcohol or ligroin. Strong acids or alkalies have no visible action on it in the cold, but short heating on the steam bath with hydrochloric acid and alcohol gave ethyl acetate with a substance described later; and on one occasion after 20 hours tetrachlorpyrocatechin. Acetic anhydride has no further action on it, and none could be detected with hydroxylamine hydrochloride. Aniline, phenylhydrazine, or benzylphenylhydrazine, even when diluted with solvents, gave tarry products, from which no definite compounds could be isolated.

Its behavior with alcohol and hydrochloric acid or with pyridine is described later.

Tetrachlorpyrocatechin Ether of 2,5-Dichlor-1,1-diacetoxycyclopentadiene, $C_6Cl_4O_2C_5(OC_2H_3O)_2Cl_2O$(?)—The mother liquors left after the crystallization of the substance prepared by the action of acetic anhydride on the nitro hemiether yielded a viscous mass on evaporation, which could not be converted into a crystalline substance by treatment with any of the common solvents. It was, therefore, dissolved in benzene and treated with pyridine, which converted the ketocyclopentadiene hemiether into the red complete ether, and this crystallized out. The filtrate from these crystals, on evaporation, left a dark viscous residue, which was heated with acetic anhydride either with or without benzene, until it turned black, and became so thick as to flow slowly even when warm, after which, on cooling, it showed a tendency to crystallize. Accordingly it was dissolved in chloroform and excess of tetrachloride of carbon added, which precipitated the tar. When the supernatant liquid had become clear, it was decanted and the liquid tar treated again with tetrachloride of carbon; this last extract was filtered off, since the treatment had made the tar too viscous to pass through the paper. The solution, on slow evaporation, deposited white crystals, which were purified by crystallization from tetrachloride of carbon and alcohol, from benzene, and from benzene and alcohol, till they showed the melting point 188°, when they were dried at 80°.

see errata, p. 548

I. 0.3095 gram substance gave 0.4101 gram CO_2 and 0.0574 gram H_2O.

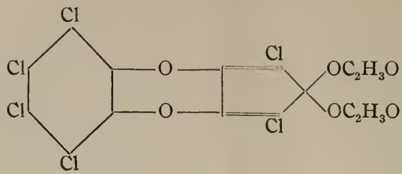
II. 0.2466 gram substance gave 0.3299 gram CO_2 and 0.0512 gram H_2O.

III. 0.1153 gram substance gave 0.2000 gram AgCl.

IV. 0.1122 gram substance gave 0.1940 gram AgCl.

	Calculated for $C_{15}H_6O_6Cl_6$	Found I	II	III	IV
C	36.36	36.14	36.49	...	...
H	1.21	2.07	2.32	...	...
Cl	43.03	...	...	42.89	42.75

Of the possible graphic formulas for this substance (XII)



(XII)

agrees best with the reactions by which it was formed, and has therefore been adopted provisionally for the purpose of indexing, but it is obvious that more work is necessary before it can be considered established. The substance is therefore the tetrachlorpyrocatechin ether of 2,5-dichlor-1,1-diacetoxy-cyclopentadiene.

Properties.—It crystallizes from a mixture of tetrachloride of carbon, or chloroform, with alcohol, in white hexagonal prisms, from benzene in long needles, from benzene and alcohol in rhombic plates. It melts at 188° to a colorless liquid; it is soluble in ether, acetone, chloroform, tetrachloride of carbon, or benzene; less soluble in alcohol or ligroin. It is not visibly affected by the three strong acids, or by alkalies even when warm.

When this compound, melting at 188°, was boiled for several hours with alcohol and an excess of hydroxylamine hydrochloride, the solid gradually went into solution. The straw-colored liquid thus obtained gave with water a white emulsion containing some brownish yellow crystals, the amount of which increased on standing. These were separated from an amorphous precipitate and crystallized from benzene and ligroin until they melted at 180°. Two analyses showed it was not pure, but that it contained over 10 per cent. more chlorine than the original compound. No test for nitrogen could be obtained after fusion with sodium, but such a negative result is not entitled to much weight. The substance seems to be the same with that melting at 180°–183° obtained in the same way from the ketone ether and described later.

Tetrachlorpyrocatechin Hemiether of Trichlorketocyclopenta-

diene, $C_6Cl_4(OH)OC_5Cl_3O$.—This compound was obtained by saponification of its acetyl compound (melting at 165°) already described, as follows: Two grams were heated with a mixture of 5 cc. of strong hydrochloric acid and 20 cc. of alcohol until the odor of ethyl acetate was no longer perceptible; then the solid, which showed no visible change, was purified by shaking with water and crystallization from benzene and alcohol, followed by benzene and ligroin. It melted, when dipped into the hot bath; at 188°, and was dried at 80°.

I. 0.1107 gram substance gave 0.2557 gram AgCl.

II. 0.1099 gram substance gave 0.2539 gram AgCl.

	Calculated for $C_{11}HO_3Cl_7$	Found I	Found II
Cl	57.86	57.13	57.43

Properties of the Tetrachlorpyrocatechin Hemiether of Trichlorketocyclopentadiene.—It crystallizes from benzene and alcohol in clusters of white needles and melts with decomposition at 182°–185°, if heated in the bath; at 188°, if dipped into the hot bath. It is freely soluble in most of the organic solvents; slightly soluble in methyl or ethyl alcohol, ether or ligroin. Strong acids or alkalies are without visible effect on it in the cold, but when heated for several hours with hydrochloric acid and alcohol, tetrachlorpyrocatechin was formed, recognized in the usual way. In spite of many attempts we did not succeed in isolating the other product of this reaction. Pyridine converts the hemiether into the red compound described in the next section, which it also forms with the acetyl body.

Tetrachlorpyrocatechin Ether of Dichlorketocyclopentadiene, $C_6Cl_4O_2C_5Cl_2O$.—This substance was obtained by the action of pyridine on a benzene solution of the corresponding heptachlor hemiether (melting at 188°), or its acetyl compound (melting at 165°). The viscous residue left after evaporation of the mother liquors obtained in purifying the last compound was an excellent source of this ether, and it first yielded us a good supply of the body, but later we failed in obtaining it in quantity, so that we were forced to leave some of our work in an unfinished condition. This is a good example of

the frequently occurring cases in this work, where processes failed to give the results obtained at first, although the conditions were kept as nearly identical as possible. When a benzene solution of one of the materials just mentioned was mixed with pyridine, the liquid darkened, then turned red, and soon bright red hexagonal plates appeared in considerable quantity. Occasionally a white product was also observed, but this disappeared on longer standing. The red crystals were purified by crystallization from benzene and alcohol, when they melted with decomposition at 264° to 272°, according to the conditions of heating. That the action in these cases consisted in the removal of hydrochloric acid or acetyl chloride by the pyridine was confirmed by studying its action on the hemiether, $C_6Cl_4(OH)OC_6Cl_3O_2$, and its acetyl compound, both of which were converted into the ether

$$C_6Cl_4O_2C_6Cl_2O_2$$

The substance melting from 264° to 272° gave the following results on analysis:

I. 0.1048 gram substance gave 0.2292 gram AgCl.
II. 0.1032 gram substance gave 0.2252 gram AgCl.
III. 0.1138 gram substance gave 0.2472 gram AgCl.

	Calculated for $C_6Cl_4O_2C_5Cl_2O$	Found I	II	III
Cl	54.19	54.08	54.12	53.71

III was prepared from the viscous residue and was known to be somewhat less pure than I and II.

Properties of the Tetrachlorpyrocatechin Ether of Dichlorketocyclopentadiene.—It crystallizes from a mixture of benzene and alcohol in very thin, bright red, hexagonal plates. The best way to obtain these is to dissolve the compound in benzene and add a quantity of alcohol, when the crystals are gradually deposited. If heated it loses color between 220° and 225°, becoming cream white, and then melts between 264° and 272°, according to the conditions of heating. The loss was determined between 225° and 240°.

I. 0.2310 gram substance lost 0.0107 gram.
II. 0.2167 gram lost 0.0100 gram.
III. 0.1352 gram lost 0.0064 gram.

	I	III	III
Loss	4.62	4.61	4.73

A loss of 18 units from the molecular weight amounts to 4.7 per cent.; but we are unable to explain the nature of this loss, as no pure compounds could be obtained from the residue, which evidently contained two products, one viscous and soluble, the other amorphous and insoluble in nearly all the common solvents. Unfortunately, our usual method of preparation failed to yield the red mother substance before we had finished the study of this reaction. The red compound is slightly soluble in the common organic solvents, more so in benzene than in the others, but not freely soluble in this. The strong acids and alkalies had no visible action on it.

Phenylhydrazine in somewhat dilute acetic acid once gave a substance crystallizing in square pyramids, but we were never able to obtain it again in spite of many attempts. When the finely powdered red compound suspended in alcohol was heated with an excess of hydroxylamine hydrochloride, it gradually went into solution, and as soon as this had happened the liquid was poured into water, which threw down an uninviting yellow precipitate, showing, however, some signs of crystals. This was purified by crystallization from benzene and ligroin, and finally from ligroin alone, which yielded ill-defined light brown crystals, softening at 178° and melting at 180°–182°. It was dried at 80°.

I. 0.2036 gram substance gave 0.2167 gram CO_2 and 0.0232 gram H_2O.

II. 0.1004 gram substance gave 0.2289 gram AgCl.

III. 0.1061 gram substance gave 0.2423 gram AgCl.

	Found		
	I	II	III
C	29.03	...	...
H	1.27	...	...
Cl	...	56.37	56.46

This substance seems to be the same as that obtained under similar conditions from the ether of the diacetoxycyclopentadiene. It cannot be the expected oxime, as that contains 52.20 per cent. of chlorine and 32.35 per cent. of carbon.

These results seem to indicate tetrachlorpyrocatechin, which contains 29.02 per cent. of carbon and 57.25 per cent. of chlorine and melts at 194°–195°, so our substance melting at 180°–182° might be an impure specimen of this substance; and this hypothesis is supported by the fact that it is turned red by nitric acid and that it is decidedly hard to purify tetrachlorpyrocatechin by crystallization from the solvents used by us.

Action of Sodic Methylate on the Tetrachlorpyrocatechin Ether of Dichlorketocyclopentadiene

Tetrachlorpyrocatechin Hemiether of the 1-Hydroxy-1,4-dimethoxydichlorcyclopentadiene,
$C_6Cl_4(OH)OC_5Cl_2OH(OCH_3)_2$.—The red compound melting at 264°–266°, suspended in a little methyl alcohol, was treated with a two per cent. solution of sodic methylate in methyl alcohol until the green substance formed at first had gone into solution, when upon acidification with dilute hydrochloric acid, and further dilution with water, an orange-colored oil was deposited. This was washed with water and then scratched with a glass rod until it changed into a crystalline mass, which was washed with successive small portions of methyl alcohol to remove viscous matter, crystallized twice from benzene and ligroin, and once from methyl alcohol, when it melted at 180°, and as the amount was too small to permit further purification, it was dried at 70° for analysis.

I. 0.1023 gram substance gave 0.1944 gram AgCl.

II. 0.1028 gram substance gave 0.1943 gram AgCl.

	Calculated for $C_{11}O_3Cl_6.2CH_3OH$	Found I	Found II
Cl	46.61	46.99	46.73

The substance is therefore formed from the ketone ether by the addition of the elements of two molecules of methyl alcohol.

Properties of the Tetrachlorpyrocatechin Hemiether of the Hydroxydimethoxydichlorcyclopentadiene.—It crystallizes in white cubes from methyl alcohol and melts with decomposition between 175° and 180°, according to the conditions of heating. It is soluble in all the common organic solvents ex-

cept ligroin. The best solvent for it is a mixture of benzene and methyl alcohol. The strong acids have no visible action on it in the cold, but hot nitric acid converts it into a red oil; sodic hydroxide solution dissolves it without change of color, and it is thrown down from this solution as a colorless oil by hydrochloric acid.

Action of Sodic Ethylate on the Tetrachlorpyrocatechin Ether of Dichlorketocyclopentadiene

Tetrachlorpyrocatechin Hemiether of the Hydroxydiethoxydichlorcyclopentadiene, $C_6Cl_4(OH)OC_5Cl_2OH(OC_2H_5)_2$.—The ether was suspended in a little alcohol and a three per cent. solution of sodic ethylate added until the green precipitate formed at first dissolved, when hydrochloric acid and water were added to complete precipitation, and the pale yellow oil thrown down was washed with water. On adding a few drops of ethyl alcohol and scratching the oil with a rod it solidified, after which it was washed with small quantities of ethyl alcohol to remove the viscous matter, and then dissolved in hot alcohol, when, after adding hot water to the solution, until the first turbidity appeared, and scratching the dish with a glass rod as it cooled, needles were obtained. The yield was small, and owing to the difficulty of preparing the mother substance, the amount of material was enough for only two analyses, the first of which was made on a specimen dried for a day *in vacuo* after being air-dried. It melted at 93°.

0.1014 gram substance gave 0.1746 gram AgCl.

	Calculated for $C_{15}H_{12}O_5Cl_6.H_2O$	Found
Cl	42.34	42.57

The specimen for the second analysis was dried at 50°.

0.1074 gram substance gave 0.1933 gram AgCl.

	Calculated for $C_{15}H_{12}O_5Cl_6$	Found
Cl	43.92	44.50

It is to be regretted that we did not have material enough to determine whether the substance dried *in vacuo* really contained a molecule of water of crystallization. A certain con-

firmation of the single analysis is given by the fact that water was used in purifying it, and that the melting point is abnormally low, 93°, whereas the methyl compound melts at 180°. The whole of the substance was used in the second analysis so that no melting point could be taken with the substance dried at 50°.

Properties of the Tetrachlorpyrocatechin Hemiether of Hydroxydiethoxydichlorcyclopentadiene.—It crystallizes from ligroin in clusters of needles, from methyl alcohol in poorly defined cubes. It melts at 93° to a pale yellow liquid, which undergoes no visible change, even when the temperature is carried up to 200°. It is soluble in alcohol, ether or benzene; insoluble in water. It melted without change of color in hot hydrochloric acid, but in the cold no visible effect was produced by the three strong acids or by sodic hydroxide solution (difference from the methyl compound).

Action of Benzoyl Chloride on the Nitrohemiethercarboxylic Acid Melting at 176°–198°

Tetrachlorpyrocatechinbenzoyl Hemiether of Trichlorketocyclopentadiene, $C_6Cl_4(OCOC_6H_5)OC_5Cl_3O$.—This reaction could be carried on with benzoyl chloride alone or diluted with toluene, but the best results were obtained by using the Baumann-Schotten method as follows: The hemiether was dissolved in acetone, and after being rendered alkaline with aqueous sodic hydroxide, benzoyl chloride in excess was added. On warming, a yellow oil was deposited which was washed with water and treated with a little alcohol, when glistening white scales appeared. These were crystallized from benzene and alcohol until they showed the melting point 172°, when the substance was dried at 100°. I and II are analyses of one preparation, III and IV of another.

I. 0.2724 gram substance gave 0.4057 gram CO_2 and 0.0440 gram H_2O.

II. 0.1093 gram substance gave 0.2055 gram AgCl.

III. 0.1191 gram substance gave 0.2229 gram AgCl.

IV. 0.0665 gram substance gave 0.1243 gram AgCl.

	Calculated for $C_{18}H_5O_4Cl_7$	Found I	II	III	IV
C	40.49	40.62	...	...	...
H	0.94	1.81	...	...	...
Cl	46.58	...	46.49	46.27	46.20

The action, therefore, with benzoyl chloride is exactly analogous to that with acetyl chloride or acetic anhydride.

Properties of the Tetrachlorpyrocatechinbenzoyl Hemiether of Trichlorketocyclopentadiene.—It crystallizes from alcohol in glistening white scales, which melt at 172° to a colorless liquid. Easily soluble in benzene, much less soluble in alcohol or ligroin. The strong acids or alkalies have no apparent action on it; and the same is true of pyridine or alcohol and hydrochloric acid, so that this benzoyl compound is much more stable than the acetyl derivative, which was attacked by both of these reagents. Hydroxylamine hydrochloride seemed to react but the product was not studied.

As acetyl chloride, acetic anhydride or benzoyl chloride decomposed the tetrachlorpyrocatechin hemiether of 2-nitro-2,4,5-trichlor-1,3-dihydroxycylcopentene-1-carboxylic acid,

$$C_6Cl_4(OH)OC_5Cl_3(OH)_2(NO_2)COOH$$

and therefore gave no means of determining the number of hydroxyls it contained, we thought of trying other methods to reach the desired result, but could find none available, since Schryver's[1] method needs 2 or 3 grams of material, which could not be provided without more labor than it was worth, and Tschugaeff's[2] method gave incorrect results in trial experiments with the ether $C_6Cl_4(OH)OC_6Cl_3O_2$, so that it was obviously not worth while to try it on our substance.

Action of Nitric Acid on the Hexachlormethoxyorthobenzoquinopyrocatechin Hemiether

Tetrachlorpyrocatechin Hemiether of Nitrodichlormethoxydihydroxycyclopentenecarboxylic Acid,
$C_6Cl_4(OH)OC_5Cl_2(OCH_3)(OH)_2(NO_2)COOH$(?)—A warm saturated solution of the hemiether in glacial acetic acid was treated

[1] J. Soc. Chem. Ind., **18**, 533 (1899).
[2] Ber. d. chem. Ges., **35**, 3912 (1902).

with three per cent. by volume of fuming nitric acid and the mixture kept at a temperature of 50° to 60° for three or four minutes, after which water was gradually added until the first permanent precipitate was formed, when, on cooling, the orange solution deposited a voluminous mass of crystalline scales. These were washed with a little water, dried at 60°, and crystallized first from benzene and methyl alcohol, later from benzene and ligroin. These solvents gave poorly defined crystals, but were more efficient than any others we could find. The purified substance melted at 202° to 208°, according to the conditions of heating. It was dried at 60°.

I. 0.1325 gram substance gave 0.2139 gram AgCl.

II. 0.1335 gram substance gave 0.2155 gram AgCl.

	Calculated for $C_{13}H_7O_9NCl_6$	Found I	Found II
Cl	39.81	39.92	39.91

The reaction is therefore analogous to that with the heptachlor hemiether.

Properties of the Tetrachlorpyrocatechin Hemiether of Nitrodichlormethoxydihydroxycyclopentenecarboxylic Acid.—It forms ill-defined, pure white crystals which melt with decomposition at 202° or 208°, according to the speed with which they are heated. It is soluble in ethyl or methyl alcohol, ether, acetone, chloroform, or benzene; very slightly soluble in ligroin; essentially insoluble in water. The best solvents are benzene and ligroin, benzene and methyl alcohol, or methyl alcohol alone. The three strong acids have no visible action in the cold; sodic hydroxide solution dissolves it without change of color. It is much more easily purified than the corresponding heptachlor compound.

Action of Acetyl Chloride or Acetic Anhydride on the Methoxy Compound Melting at 202° to 208°.—When this substance was heated for one hour with several times its weight of acetyl chloride, hydrochloric acid was given off in quantity, in fact the evolution started even in the cold. The cooled solution was poured into a large volume of cold water, which precipitated a viscous material, and this, when kneaded under water, became granular, and after crystallization from benzene and

ligroin melted with effervescence at from 195° to 215°. Two chlorine determinations indicated that the substance was the original compound (40.02 and 39.98 instead of 39.81 per cent.), in spite of the difference in decomposition points. It seemed, therefore, that an acetyl compound had been formed which was afterward decomposed by the water.

In a second experiment a mixture of the methoxy compound and an excess of acetyl chloride was heated for 4 hours instead of one. The precipitate with water was dirty white, and after being rendered granular by kneading with water was crystallized from methyl alcohol till it was white and melted between 150° and 170° (I and II). What seemed to be the same product was obtained by heating the methoxy compound with 10 times its weight of acetic anhydride on the steam bath for half an hour. On cooling, it was treated with methyl alcohol and evaporated on the steam bath, after which it was crystallized from benzene and methyl alcohol till it was white and melted at 146° (this lower point is probably due to differences in the conditions of heating). It was dried at 60° (III and IV).

I. 0.2193 gram substance gave 0.2570 gram CO_2 and 0.0444 gram H_2O.

II. 0.1140 gram substance gave 0.1697 gram AgCl.

III. 0.1071 gram substance gave 0.1589 gram AgCl.

IV. 0.1134 gram substance gave 0.1681 gram AgCl.

	Calculated for $C_{15}H_9O_{10}NCl_6$	Found I	II	III	IV
C	31.25	31.96	...	...	...
H	1.56	2.26	...	...	...
Cl	36.94	...	36.81	36.68	36.65

The reaction, therefore, has consisted in the introduction of one acetyl group without the deep-seated decomposition observed during the similar treatment of the corresponding heptachlor hemiether.

Properties of the Tetrachlorpyrocatechinacet Hemiether of Nitrodichlormethoxydihydroxycyclopentenecarboxylic Acid.—It crystallizes from benzene and alcohol in clusters of white needles, from hot methyl alcohol in plates. When heated rapidly it

usually melts at 146° with decomposition, but if heated for some time at 110°, it is converted into another substance, which does not melt below 190°. A specimen heated to 105° for fifteen hours lost 7.7 per cent.; it was then accidently overheated, so that the residue could not be studied, and it was not certain that the loss was constant. This would amount to a loss of 44 units from the molecular weight. The acetyl compound is soluble in acetone, chloroform, tetrachloride of carbon or benzene; less soluble in methyl alcohol; essentially insoluble in water. With the three strong acids, or sodic hydroxide, no visible action is observed in the cold.

Methyl alcohol and sulphuric acid heated with the methoxy compound for 15 minutes had little action upon it, most of the original substance being recovered unchanged. We regret that lack of time prevented us from repeating the experiment with longer heating, as oxides of nitrogen began to come off toward the end of the 15 minutes.

Action of Nitric Acid on Hexachlorethoxyorthobenzoquinopyrocatechin Hemiether.—The ethoxy compound,

$$C_6Cl_4(OH)OC_6Cl_2(OC_2H_5)O_2$$

was dissolved in the least quantity of hot glacial acetic acid and the solution cooled to about 60° and treated with from 3 to 5 per cent., by volume, of fuming nitric acid. The mixture was kept at about 60° for five minutes, and then hot water was added until a slight turbidity appeared, after which, on cooling, a voluminous white precipitate was thrown down, and this was washed with water. A second compound, described later, was obtained from the filtrate and wash waters. The precipitate, after drying at 50°, was crystallized from benzene and ligroin, until it melted at 214°–215°, when it was dried at 70°. Analysis I was made with one preparation, II and III with another.

I. 0.1063 gram substance gave 0.1730 gram AgCl.

II. 0.1079 gram substance gave 0.1736 gram AgCl.

III. 0.1177 gram substance gave 0.1911 gram AgCl.

	Calculated for $C_6Cl_4(OH)OC_6Cl_2(OC_2H_5)O_2.HNO_3$	Found I	II	III
Cl	40.19	40.24	39.78	40.15

In the absence of sufficient data for assigning a structural formula to this substance it may be called the mononitric acid compound of the tetrachlorpyrocatechin hemiether of ethoxydichlororthoquinone.

Properties.—It separates from glacial acetic acid and water in glistening white scales; from benzene and ligroin in rhombic prisms; from tetrachloride of carbon in rhombic plates; thus, unlike the related compounds, it forms well defined crystals. It melts with effervescence at 210° or 215°, according to the speed with which it is heated. It is soluble in alcohol, ether, chloroform, tetrachloride of carbon or benzene; slightly soluble in ligroin; essentially insoluble in water. The strong acids have no apparent action on it in the cold; sodic hydroxide solution dissolves it, and acids give an oily precipitate with this solution; ammonic hydroxide dissolves it less easily, forming a yellow solution.

Dinitric Acid Compound of the Tetrachlorpyrocatechin Hemiether of Ethoxydichlororthoquinone.—The filtrate and wash waters from the preparation of the compound just described were mixed and allowed to stand, when white rhombic crystals in small amount were deposited, which were analyzed without further purification.

I. 0.1060 gram substance gave 0.1544 gram AgCl.

II. 0.1076 gram substance gave 0.1577 gram AgCl.

	Calculated for $C_6Cl_4(OH).O.(C_2H_5O)C_6Cl_2O_2(HNO_3)_2$	Found I	II
Cl	35.91	36.02	36.24

Although these results agree very well with the formula given, it is obvious that more analytical data are necessary before it can be accepted definitely.

The substance crystallizes from dilute acetic acid in white rhombic prisms, which when dipped into the hot bath melt at 145° with effervescence; if heated in the bath it softens at 130°, but then does not melt completely until 158°. It is soluble in alcohol, ether, chloroform, tetrachloride of carbon or benzene; slightly soluble in ligroin; essentially insoluble in water. The strong acids produce no visible change in the cold; sodic hydroxide dissolves it partially, but without change of color.

Cambridge, Mass.
March 14, 1913

ON THE REACTIONS OF BOTH THE IONS AND THE NONIONIZED FORMS OF ELECTROLYTES

THE REACTIONS OF SODIUM PHENOLATE WITH METHYL IODIDE AND ETHYL IODIDE IN ABSOLUTE ETHYL ALCOHOL AT 25° AND 35°

By H. C. Robertson, Jr., and S. F. Acree

[SEVENTEENTH[1] COMMUNICATION ON CATALYSIS]

(We are indebted to the Carnegie Institution of Washington for aid in these researches.)

In 1905 Brunel and Acree began an investigation to learn whether in all ordinary, and catalyzed, chemical reactions involving electrolytes (acids, bases and salts) the ions as well as the nonionized forms are concerned. The fundamental investigations of Arrhenius[2] and Ostwald[3] and their students had placed the ionization theory on a sound footing, but had, perhaps unfortunately, also led chemists, with a few exceptions,[4] to believe that the *ions* are the only portions of electrolytes capable of entering into transformations.[5] The very

[1] This Journal, **27,** 118; **28,** 370; **31,** 185; **32,** 606; **37,** 71, 361; **38,** 1, 258, 489, 746; **39,** 124, 145, 226, 300; **41,** 457, 483; **42,** 115; **43,** 358, 505; **44,** 219; **48,** 352; **49,** 116, 345, 369. Ber. d. chem. Ges., **33,** 1520; **35,** 553; **36,** 3139; **37,** 184, 618; **41,** 3199. Science, **30,** 617 (1909). J. Am. Chem. Soc., **30,** 1755. Dr. Robertson did this work in 1909 and 1910 and presented it as a dissertation for the Ph.D. degree in June, 1910. A few notes have been added by one of us to bring the work up to date, but the fundamental conclusions have not been changed.—S. F. A.

[2] Z. physik. Chem., **1,** 110, 631; **2,** 284; **4,** 226; **28,** 217, 326.

[3] J. prakt. Chem., [2] **27,** 1; **28,** 449; **29,** 406; **30,** 231; **31,** 307; **33,** 352; **35,** 112. Z. physik. Chem., **2,** 36, 136, 270.

[4] See especially Kahlenberg: J. Phys. Chem., **5,** 339; **6,** 1. Michael: This Journal, **43,** 322. Stieglitz: Cong. Arts and Sciences, St. Louis, 1904, and later papers. Acree: This Journal, **37,** 410; **38,** 258, and later papers.

[5] In recent years the application of these quantitative ideas to organic reactions has been used very successfully by a number of workers. In front rank stands the work of Stieglitz (This Journal, **39,** 29, 166, 402, 437, 586, 719. J. Am. Chem. Soc., **32,** 221; **34,** 1687. Congress Arts and Sciences, St. Louis, 1904) on the imido esters and their salts and his proof that the ions and nonionized substances are active. Especially important was his correlation of this work with the general problems of catalysis. Bredig (Z. Elektrochem., **9,** 118; **10,** 586; **11,** 528; **18,** 535, 539. Z. physik. Chem., **47,** 185) made a number of studies which he interpreted as reactions of ions, the best of which were perhaps his study of the catalysis of hydrogen peroxide by iodide ions, and of the decomposition of diazoacetic ester by hydrogen ions. The relation of this to the catalysis of esters through the activity of complex oxonium salts was discussed by him. Goldschmidt's work (Z. Elektrochem, **15,** 6. Z. physik. Chem., **60,** 728; **70,** 627; **81,** 30. Ber. d. chem. Ges., **39,** 711) on the esterification of organic acids

brilliancy of the new idea, together with the *apparent* evidence, and the authority of Arrhenius and Ostwald, dazzled chemists to such an extent that the possible activity of the nonionized substances was almost entirely neglected. When we began our work there was already some evidence that both the ions *and the nonionized forms* of acids, bases and salts are concerned in the well-known saponification of esters by acids and alkalies, in the inversion of cane sugar by acids, in the decomposition of diacetone alcohol by alkalies, in the formation of benzoin from benzaldehyde by potassium cyanide, in the inversion of menthone by sodium ethylate, in the rearrangement of acetylchloroaminobenzene by acids through the activity of the nonionized salt,

$$CH_3CONHClAnC_6H_5\ (An = Cl, Br)$$

and other cases discussed[1] in previous articles. All of these reactions had been assumed by others to involve only the hydrogen ions of the acid, the hydroxyl ions of the bases, or similar mechanisms.

The experimental evidence in all of these cases being in such condition that it could not be analyzed with absolute certainty, and the important factor of "salt catalysis" being so little understood, we deemed it wise to undertake the study of some typical organic reactions *in absolute ethyl alcohol* in order to measure all of the necessary factors with as high a degree of precision as possible. Ethyl alcohol was chosen as the solvent because in it the per cent. of ionization of different substances *varies far more* than in water, when the solutions are diluted from N/1 to N/2048. This fact is of the very greatest importance in studying the activity of the *nonionized electrolytes*, because *in N/1 alcoholic solutions, for instance, the concentration of the nonionized electrolyte is several times that found in the corresponding aqueous solutions, and the ac-*

in absolute ethyl alcohol proved the same general ideas and has formed, on account of its wealth of detail, one of our most important chapters. The work of Lapworth (J. Chem. Soc., **93**, 2163, 2203; **97**, 21; **99**, 1417, 2224; **101**, 2249; **103**, 252) on the influence of small amounts of water on esterification, conductivities, electromotive forces, and vapor pressures has formed one of our most brilliant chapters, because it furnished a much needed and far-reaching coördination of the physical properties and chemical activity of solutions, an example which should be followed by all chemists.

[1] For references see This Journal, **48**, 352; **49**, 348.

tivity of the nonionized electrolyte is therefore easily measured in most cases studied by us.

We chose a few typical organic reactions for study, in some of which an electrolyte, for example an ethylate, was involved *purely catalytically* and was not decomposed during the chemical transformations, but in others of which the electrolyte was completely transformed into the end products. Such widely different cases were chosen to allow us to see whether the mechanism of the reaction is the same in both cases, both ions and nonionized electrolytes being involved alike in both classes of reactions. Our study of the *pure catalysis* of the reversible reaction

$$NaOC_2H_5 + RC:N + C_2H_5OH \rightleftarrows NaOC_2H_5 + RC(:NH)OC_2H_5$$

by sodium, potassium and lithium ethylates, in which the ethylates are not changed into the end products, has shown that the mechanism of this reaction is essentially the same as that involving the sodium, potassium and lithium ethylates and methyl iodide or ethyl iodide, in which, of course, the ethylate is transformed into the end products:

$$C_2H_5ONa + IC_2H_5 \longrightarrow (C_2H_5)_2O + NaI$$

The evidence shows that the ethylates react in both cases through their ethylate ions as well as through their nonionized forms.

Another class of reactions studied by us and described in part in the present communication, and which have been found to be quite analogous to those involving ethylates and alkyl halides, are the changes involved when alkyl halides react with sodium, potassium and lithium phenolates in absolute ethyl alcohol:

$$C_6H_5ONa + ICH_3 \longrightarrow NaI + C_6H_5OCH_3$$

$$C_6H_5\overline{O} + ICH_3 \longrightarrow \overline{I} + C_6H_5OCH_3$$

The reactions proceed smoothly at 25° and 35° and the constants remain very regular throughout a large part of the transformation. The constants become from 3 to 5 per cent.

smaller toward the end of the change, probably because some of the alkyl halide may escape through the stoppers closing the flasks containing the reaction mixture, because the ether and sodium halides formed in the reaction suppress the ionization of sodium phenolate slightly, because there is probably a slight catalysis by the sodium halide formed, and especially because a small amount of the alkyl halide may form an olefin by a monomolecular reaction.[1] We have, therefore, disregarded at present the small decrease in the constants toward the end of the reaction and have considered the apparent course of the main reaction, which certainly seems to be bimolecular. We shall, however, study especially the side reaction involving the formation of olefins, along with the others.

In developing the equations[2] which we should use we may consider the case first in which the alkyl halide reacts with the phenolate anion. If these unite to form a complex anion in very *small traces*[3] and we represent the concentrations by the formulas, the equation

$$(a)\ CH_3I \times \overline{An} = K \times CH_3I.\overline{An}$$

holds *approximately* for any given concentrations even though the value of the "stability constant" K is not constant for all concentrations. We cannot experimentally[4] measure K at present and our only reason for thinking that K should remain constant for all concentrations is that the stability constants of most complex salts, such as double cyanides, complex ammonium salts, etc., are fairly constant. If this complex

[1] Brussoff (Z. physik Chem., **34**, 129) found that ethyl iodide and potassium hydroxide in ethyl alcohol at 78° form 16 per cent. of ethylene.

[2] The K_i and K_m used here may be the sum or product of other constants and may be made to include "salt effects" of ions or molecules; the "salt effect," however, seems fortunately to be small in this case.

Since it has been shown by Carrara (Gazz. chim. ital., **26**, I, 119; **33**, I, 241. Ahren's Sammlung, **12**, 403. Lapworth and Partington: J. Chem. Soc., **99**, 1417) that the ionic mobilities of sodium, potassium and lithium salts hardly change with concentration we shall assume, until our further work is completed, that $\alpha = \mu_v/\mu_\infty$ and that $\alpha(A - x)$ represents the ionic concentration of the sodium phenolate or sod um ethylate.

[3] For the development of these equations see Johnson and Acree: This Journal, **37**, 410; **38**, 258; **43**, 519; **48**, 352. Ber. d. chem. Ges., **41**, 3210, par. 1 and footnote 1, and p. 3214, par. 2, and other articles.

[4] We have planned some experiments to measure K.

yields the end products the following equations hold approximately, whether the complex salt is formed slowly (either reversibly or irreversibly) and decomposes rapidly, or is formed rapidly reversibly and decomposes slowly:

$$
\begin{aligned}
(b)\quad dx/dt &= K'_i \times CH_3I.An \\
&= K'_i/K \times CH_3I \times An \\
&= K_i \times CH_3I \times An
\end{aligned}
$$

But this is exactly the same equation that we get if the alkyl halide and anion react directly without the formation of an intermediate complex anion. In the one case our reaction velocity constant K'_i/K is the quotient of two constants, both of which (or the quotient) are assumed to be constant for all concentrations; in the other case we make no assumptions other than the constancy of the reaction velocity K_i.

In the present studies, however, the above equation fails to represent the entire reaction, and we may therefore consider the possibility of reactions of nonionized substances. It might well be that the *nonionized* double salt $C_2H_5I.NaOC_6H_5$ can decompose *in solution* into sodium iodide and phenyl ethyl ether just as Scholl[1] and Steinkopf have shown the *solid* (and presumably *nonionized*) cyanomethyl iodide-silver nitrate double compound to yield silver iodide and cyanomethyl nitrate. We may consider this nonionized double salt to be formed by the union of the alkyl halide with the anions and cations of the sodium phenolate, or by the union of the alkyl halide and nonionized sodium phenolate. These two processes are represented as follows:

$$(c)\quad C_2H_5I \times \overset{-}{O}C_6H_5 \times \overset{+}{Na} = K' \times C_2H_5I.NaOC_6H_5$$

and

$$(d)\quad C_2H_5I \times NaOC_6H_5 = K'' \times C_2H_5I.NaOC_6H_5$$

It is clear that if sodium phenolate obeyed Ostwald's dilution law, and the equation

$$\overset{+}{Na} \times \overset{-}{O}C_6H_5 = K''' \times C_6H_5ONa = \frac{K'}{K''} \times C_6H_5ONa$$

were true for all concentrations, K' and K'' also being constant,

[1] Ber. d. chem. Ges., **39**, 4393. Hantzsch and Caldwell: *Ibid.*, **39**, 2472. Acree and Loy: This Journal, **45**, 224.

we could not possibly tell which of these two processes is taking place. The reaction (*c*) would be written

$$(e)\quad dx/dt = K_m \times C_2H_5I.NaOC_6H_5$$
$$= K_m/K'C_2H_5I \times OC_6H_5 \times Na$$
$$= \frac{K_m K'''}{K'} \times C_2H_5I \times NaOC_6H_5 =$$
$$\frac{K_m}{K''} \times C_2H_5I \times NaOC_6H_5$$

Equation (*e*) also represents the catalysis, by the sodium ions, of the reaction between the alkyl halide and the phenolate ions.

The reaction (*d*) would be written

$$(f)\quad dx/dt = K_m \times C_2H_5I.NaOC_6H_5$$
$$= \frac{K_m}{K''} \times C_2H_5I \times NaOC_6H_5$$

which would also hold even if no complex salt were formed as an intermediate product. If the sodium phenolate obeyed the Ostwald dilution law these two equations could be used interchangeably and we could not know whether the sodium phenolate reacts through the sodium and phenolate ions together, or through its nonionized portion, or through both processes together, and we could not know whether a *negligible trace* of the complex salt is an intermediate product.

Sodium phenolate apparently does not obey Ostwald's dilution law and these equations (*e*) and (*f*) are not identical by any means. If Equations (*b*) and (*c*) represent the true reactions the total reaction can be represented by the Equation (g) if α is the ionization and $(A - x)$ is the concentration of the sodium phenolate, and $(B - x)$ is the concentration of the alkyl halide at time t and $x = o$ when $t = o$.

$$dx/dt = K_i\alpha(A-x)(B-x) + K_m\frac{\alpha^2}{V}(A-x)(B-x)$$
$$= \left[K_i\alpha + K_m\frac{\alpha^2}{V}\right](A-x)(B-x), \text{ or}$$
$$(g)\qquad K_V = \left[K_i\alpha + K_m\frac{\alpha^2}{V}\right]/V = \frac{B}{t(A-B)}\ln\frac{B(A-x)}{A(B-x)}$$

The Equation (h) holds if Equations (b) and (f) represent the two side reactions:

$$(h)\quad dx/dt = K_i\alpha(A-x)(B-x) + K_m(1-\alpha)(A-x)(B-x)$$
$$= [K_i\alpha + K_m(1-\alpha)](A-x)(B-x), \text{ or}$$
$$K_V = [K_i\alpha + K_m(1-\alpha)]/V = \frac{B}{t(A-B)} \ln \frac{B(A-x)}{A(B-x)}$$
$$= \frac{x}{t(A-x)}$$

when the concentrations of the sodium phenolate and alkyl halide are equal. Therefore

$$VK_V = K_N = K_i\alpha + K_m\,(1-\alpha)$$

for normal solutions of ionization α when $1/V$ is the concentration of the sodium phenolate.

It may be stated at once that Equation (g) has led to satisfactory constants in only two cases, those of the reactions between methyl iodide and sodium ethylate and potassium ethylate, whereas Equation (h) gives satisfactory constants in all of the cases studied up to this time. Whether in those two particular cases the methyl iodide does react with both ions together, perhaps along with the nonionized molecules, or whether it is an arithmetical accident cannot be said at present. Since some other hypotheses have not yielded satisfactory constants we shall confine ourselves at present to the discussion of Equation (h).

It is evident, then, that when the reaction velocities and ionic concentrations are measured in various solutions we have variations in K_N, α, $(1-\alpha)$, A and B. We can therefore determine the values of K_i and K *for normal solutions* from the series of simultaneous equations,

$$K_N = K_i\alpha + K_m(1-\alpha)$$
$$K'_N = K_i\alpha' + K_m(1-\alpha')$$
$$K''_N = K_i\alpha'' + K_m(1-\alpha''), \text{ etc.}$$

which are obtained by equating the values of K_N observed against the corresponding values of $K_i\alpha + K_m(1-\alpha)$, and substituting the proper values in Robertson's equations,

$$K_m = \frac{K_N\alpha' - K'_N\alpha}{\alpha' - \alpha}$$

and

$$K_i = \frac{K'_N(1-\alpha)-K_N(1-\alpha')}{\alpha'-\alpha}$$

These two equations make it clear at once that K_m becomes zero when K_N is proportional to the ionic concentration of the salt. That is, if

$$K'_N : K_N = \alpha' : \alpha \quad \text{or} \quad K'_N\alpha - \alpha' K_N = 0$$

then

$$K_m = \frac{K_N\alpha' - K'_N\alpha}{\alpha'-\alpha} = \frac{0}{\alpha'-\alpha}$$

Similarly, K_i becomes zero when K_N is proportional to the molecular concentration of the salt $(1-\alpha)$. That is, if

$$K'_N : K_N = (1-\alpha') : (1-\alpha)$$

then

$$K'_N(1-\alpha) - K_N(1-\alpha') = 0$$

and

$$K_i = \frac{K'_N(1-\alpha)-K_N(1-\alpha')}{\alpha'-\alpha} = \frac{0}{\alpha'-\alpha}$$

Similarly, if $K_m = K_i$, then it follows that $K_N = K'_N$ and the velocity of the reaction, when referred to normal solutions, will not change with change in concentration.[1] In this case we find that $K_i = K_m = K_N$.

When we determine experimentally, with accuracy, the values of K_i and K_m by using two solutions of different concentrations we can calculate the reaction velocity at any other concentration. Smaller errors are involved when these two concentrations differ as widely as is experimentally advisable, the difference $\alpha' - \alpha$, etc., being then larger and smaller errors appearing in K_i and K_m. It is seen in Table XXVI that when N/1 and N/32 solutions are compared the values 0.0283 and 0.00476 are obtained for K_i and K_m, respectively, the average of all the values being 0.0282 and 0.00474. This agreement is excellent, but no better than was obtained in all the other work with other phenolates, and with sodium, potassium and lithium ethylates to be reported in another article.

[1] This case is approached closely in certain cases involved in the catalytic inversion of menthone by sodium ethylate, and the addition of alcohol to nitriles in the presence of sodium, potassium, lithium and tetramethylammonium ethylates, on which we shall report soon.

All the possible combinations have been used in determining K_i and K_m and the results are given in Tables XXVI and XL for methyl iodide at 25° and 35°, and Tables LIII and LXIV for ethyl iodide at 25° and 35°. As can be seen, the variation in the values obtained for K_i and K_m is considerable, those for K_i in Table XXVI varying between 0.0264 and 0.0300 and those for K_m varying between 0.000372 and 0.00574 in the case of the reactions with methyl iodide at 25°, and those for K_i and K_m at 35° varying in a similar manner. This variation of about 50 per cent., in some cases, in the values of K_i and K_m may seem to indicate a very large experimental error in the determination of the reaction velocity, K_N, or the per cent. of ionization, α, of the phenolate salt, but such is not the case; the form of the equations, in which small differences, $\alpha' - \alpha$, etc., appear, is really responsible for such apparently large errors. The following example will illustrate the point: In Table XXV we find the values 0.01272 and 0.01447 for K_N for N/8 and N/16 solutions of sodium phenolate and methyl iodide at 25°. These values give 0.00574 as the value of K_m in Table XXVI. But if the values 0.01259 and 0.01462 had been used for K_N, the first being *decreased* therefore only 1.00 per cent. and the second being *increased* only 1.00 per cent., the value 0.00449 would have been found for K_m, which is *22 per cent. smaller* than the value 0.00574 actually obtained. It is perfectly apparent, then, that in this phenolate work, in which K_i is about six times as large as K_m, very small errors in K_N and α appear greatly magnified in the variations of K_i and K_m. In the work on the sodium ethylate, however, in which $K_i = 2.13\ K_m$ for methyl iodide, an error of one per cent. in K_N makes an error of only about 10 per cent. in K_m. For that reason there is much less variation in the individual values of K_i and K_m for sodium ethylate and methyl iodide, as can be seen in another article dealing with these substances.

It is best, therefore, to use (1) the average of *all* the values obtained for K_i and K_m, or (2) the average of the more accurate *starred* values obtained in those equations in which

$\alpha' - \alpha$ is larger, or (3) to combine all the simultaneous equations into one having the form

$$K_N + K'_N + K''_N + \ldots\ldots =$$
$$K_i(\alpha + \alpha' + \alpha'' \ldots\ldots) + K_m(1 - \alpha + 1 - \alpha' + 1 - \alpha'' + \ldots)$$

with which the individual equations are compared to get the values of K_i and K_m, and call these the closest approximation to the *true values*. It is seen in Table XXVI that the values obtained for K_i and K_m by these different methods all agree very closely. The values obtained for K_i and K in Tables XXVI, XL, LIII and LXIV were averaged and the average values substituted in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$. In this way "calculated" values for K_N at every concentration were obtained and these are compared with the "found" values of K_N in Tables XXVII, XLI, LIV and LXV. It will be seen that the calculated and observed values are fairly concordant, agreeing almost within the limit of experimental error. This agreement is seen to be satisfactory when we recall that in these reactions in which the K_i is much greater than K_m small errors in the measurement of K_N cause great variations in the other two constants.

It is seen from Tables XXVI, XL, LIII and LXIV that sodium phenolate reacts with methyl iodide and ethyl iodide at 25° and 35° in a way that accords with the above equations. The values obtained for methyl iodide are $K_i = 0.0282$ and $K_m = 0.00474$ at 25° and $K_i = 0.091$ and $K_m = 0.0131$ at 35°, while the data for ethyl iodide are $K_i = 0.0056$ and $K_m = 0.00099$ at 25° and $K_i = 0.0184$ and $K_m = 0.00323$ at 35°.

If this theory is correct all phenolates should react with methyl and ethyl iodides in such a way that *the same value for K_i, after it is freed of all disturbing physical and "salt" effects, should be obtained for unit concentrations of a given alkyl halide and the phenolate ion, whatever its source, whereas different values could be found for K_m, the activity of the alkyl halide and the nonionized phenolate salt.* The nonionized sodium, potassium and lithium phenolates are *different substances* and can therefore *react with different velocities* with

methyl iodide or ethyl iodide. Now the best evidence for the validity of this theory is that the application of these equations to the data obtained by the use of all three of these phenolates gives us *nearly the same values* for K_i but *different values* for K_m.

Mr. J. H. Shrader has completed a series of investigations on potassium and lithium phenolates at 25° and 35° and finds values for K_i and K_m for methyl iodide and ethyl iodide which accord excellently with our data. A résumé of all the constants is given here:

Methyl Iodide and Different Phenolates at 25°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.0282	0.0047
Mr. Shrader	Potassium phenolate	0.0283	0.0037
Mr. Shrader	Lithium phenolate	0.0289	0.0039

Methyl Iodide and Sodium Phenolate at 35°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.091	0.0131

Ethyl Iodide and Different Phenolates at 25°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.0056	0.00099
Mr. Shrader	Potassium phenolate	0.0052	0.00101
Mr. Shrader	Lithium phenolate	0.00534	0.00091

Ethyl Iodide and Different Phenolates at 35°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.0184	0.00323
Mr. Shrader	Potassium phenolate	0.0197	0.00270
Mr. Shrader	Lithium phenolate	0.0174	0.00319

When all of the data are analyzed carefully, and we consider the possibility of an "abnormal salt effect," and the fact that the results were obtained by two different workers, with different samples of materials, and different apparatus, and we remember especially the fact that relatively small experimental errors in K_N make large differences in K_i and K_m, as discussed on page 482, we see that the corresponding values for K_i agree well within the experimental errors. The values

for K_m vary considerably in many cases, in accordance with the theory. As we pointed out before, all of our work on the action of ethyl bromide, ethyl iodide and methyl iodide on sodium, potassium and lithium ethylates and on sodium phenyl-3-thiourazole harmonizes with the above experimental results and theory. We shall publish the details of all these investigations as quickly as possible.

The Study of Salt Catalysis

There is only one further point that needs discussion. It is seen from the foregoing pages that the reactions of sodium phenolate are not purely ionic, this transformation of the ions proceeding side by side with another involving, we believe, the nonionized salt. This deviation has been explained by Spohr[1] and Arrhenius,[2] and later by Lunden,[3] Euler,[4] Stieglitz,[5] and perhaps others, as an "auto effect" of the salt on the solvent or solution. We do not agree entirely with these workers and have explained our "salt catalysis" as due *chiefly* to the activity of the *nonionized salts* (the "normal" effect), augmented by a small "abnormal salt catalysis" resulting from changes in the physical properties of the solutions, and perhaps due partly to double compounds and to some role which electrons play. We are studying the question of "normal" and "abnormal" "salt catalysis" in connection with all these reactions, and we shall report our work later in detail when we study the reactions in concentrations varying from N/1 out to N/2048, especially in the presence of added salts. If there is an "abnormal salt effect" produced by the reacting phenolates, or metallic halides formed during the transformation, and such an effect can be analyzed by the equations

$$dx/dt = [1 + (f)C_{\text{salt}}][K_i\alpha + K_m(1-\alpha)] \\ (C_{\text{salt}} - x)(C_{\text{alkyl halide}} - x)$$

in which $(f)C_{\text{salt}}$ is a function of the total salt (or its ions) as

[1] J. prakt. Chem., [2] **32,** 32; **33,** 265. Z. physik Chem., **2,** 194.

[2] *Ibid.*, **1,** 110; **4,** 226; **31,** 197.

[3] *Ibid.*, **49,** 195.

[4] *Ibid.*, **32,** 348. Ber. d. chem. Ges., **39,** 2726.

[5] *Loc. cit.*

expressed first by Spohr, Arrhenius and others, the correction of K_i and K_m for $(f)C_{\text{salt}}$ must be either negligible in *nearly all* of the above reactions or have the same general order of magnitude for all three salts and the same alkyl halide. Even if the latter is the case, no surprise should be occasioned if we remember the fact that the physical properties of the corresponding solutions of all the salts concerned are very much alike.

We should lay especial stress on the fact that we have obtained results from our study of "salt catalysis" in both *concentrated* and *dilute*, or *ideal*, *solutions* which make entirely insufficient all theories proposed hitherto to explain the peculiar effect which some neutral salts have on some reactions, but not on others. We prefer, therefore, to reserve for the future our final discussion of salt catalysis, and define later the actual form of the expression $(f)C_{\text{salt}}$ used above.

EXPERIMENTAL

Introduction

Conrad and Brückner[1] have already studied the reactions of sodium phenolate with alkyl halides, but their work with these compounds was not very extensive. The methods used by them in their study of reaction velocities have been somewhat modified in details which seemed to involve sources of error. These investigators, having made up solutions of phenolates and of alkyl halides of the desired strength, mixed their entire solutions at one time in a large flask and, at the expiration of the desired time-period, pipetted out portions and titrated these. This procedure necessitated opening the flask containing the reaction-mixture a number of times and produced a loss of the volatile alkyl halide, particularly at the relatively high temperatures. It has seemed preferable to vary this procedure and carry out each individual reaction in a separate small flask of a capacity only slightly larger than the volume of solution to be introduced. In this way possible loss of alkyl halide by volatilization is avoided.

Solutions of sodium phenolate were made up as follows: A

[1] Z. physik. Chem., **3**, 450; **4**, 273, 631; **5**, 289; **7**, 274, 283.

solution of sodium ethylate having twice the strength desired for the sodium phenolate was prepared by removing the crust from sodium under ligroin, removing the ligroin by dipping small pieces into alcohol a few seconds, and then dissolving this clean sodium in absolute alcohol at 0° in a graduated flask. After the solution was brought to the proper temperature, the proper titrations with standard acid and methyl orange, and the necessary dilution with absolute alcohol, gave the solution of desired strength. A solution of similar concentration of dry phenol in alcohol was also prepared. By mixing equal volumes of the two solutions, a solution of sodium phenolate of the desired strength was obtained. The contraction on mixing the two solutions is very small, but any decrease in volume may be made up for by diluting to the mark of the flask with alcohol, if a calibrated measuring flask is used to receive the mixed solutions.

Conrad and Brückner, in studying the reactions of phenolates, made up their solutions in a similar way. They assumed, however, that when sodium ethylate is mixed with its molecular equivalent of phenol, the reaction takes place as below:

$$C_2H_5ONa + C_6H_5OH \rightleftarrows C_6H_5ONa + C_2H_5OH$$

and that the reverse reaction is inappreciable.

It was found, however, in the present investigation, that such is probably not the case.[1] On mixing equivalents of sodium ethylate and phenol, solutions of sodium phenolate were obtained which did not give satisfactory constants when reacting with alkyl halides. There was a steady though slight decline in the reaction velocity even in short time-periods. Tables I and II illustrate this fact. The logical conclusion is that not all of the sodium ethylate has been converted into phenolate, and that we have the two substances reacting at the same time with the alkyl halide. Since the velocity con-

[1] The variation of the per cent. of alcoholysis with the change in concentration has not been studied carefully enough to allow us to make these slight corrections in the work reported here. This subject is being investigated as fully as possible. Mr. Shrader has already made a study of the velocity of reaction of methyl iodide with mixtures of sodium phenolate and sodium ethylate, the latter, of course, because of its higher ionization, suppressing the alcoholysis of the sodium phenolate more effectively than does the phenol.

stant of sodium ethylate is about three times that of the phenolate, it disappears more rapidly. This would account for the decrease observed. The phenol liberated suppresses largely the further alcoholysis of the phenolate, and the constants for the longer time-periods are about the same as those obtained when 1 or 2 per cent. excess of phenol was present in the original phenolate solution.

It was found that on the addition of an excess of phenol better constants were obtained. This is noticeable when only 1 per cent. excess is added (Tables XIII and XIV). On comparing these values, however, with those in which no excess of phenol is used, we see that the former are somewhat lower in numerical value. This led to the addition of more phenol and it was found that the decrease in the velocity constant was very great when large quantities of phenol were added. Tables I to X and XIII and XIV show the effects obtained by the addition of from 1 per cent. to 30 per cent. excess of phenol.

A study of the rise in boiling point caused by the addition of varying excesses of phenol to a normal solution of sodium phenolate in absolute alcohol has been made. This should throw light on the subject by showing whether or not there is a double salt formation when an excess of phenol is added to the solution of sodium phenolate. It was found that there was no appreciable amount of double salt present at the boiling temperature of the solution since the rise of boiling point was nearly proportional to the molecular excess added. It is possible that some double salt might be present at the temperatures at which the reactions were carried out and that this is almost completely broken down at the boiling temperature. The question will be investigated further. A study of the change in viscosity, caused by the addition of varying excesses of phenol, must be made before any explanation of the phenomenon can be attempted.

In Table XI we have given figures to show the relation between the velocity of reaction and the excess of phenol. The data are derived from Tables I to X and XIII and XIV, on the assumption that one per cent. of free phenol lowers the reaction velocity about 0.75 per cent. These values are all

for 0.5 N solutions of sodium phenolate and methyl iodide at 25°.

It seems that, in preparing solutions of sodium phenolate as described above, it is necessary to add at least a slight excess of phenol in order to convert all the sodium ethylate into phenolate. *In all our reactions we have therefore added an excess of one per cent. over the calculated quantity of phenol.* It is seen from Tables I and XV that the numerical values of the velocity constants are only slightly and consistently lowered by the addition of this small excess. We shall consider this subject again in our reports on the reactions in very dilute solutions.

Probable Causes for the Decrease in Velocity Constants as the Reactions near Completion

In practically all the reactions of the alkyl halides that have been studied it has been found that there is a steady, though slight, decrease in the velocity constants as the reaction progresses. It is seldom possible to obtain concordant values after fifty per cent. of the reacting substances have undergone change. It will be seen from our tables that we have relied mainly on the first half of the reactions for the best constants. The cause of this decrease in velocity constants has been attributed by many investigators to a loss of alkyl halide during the course of the reaction. The question has been taken up in the present investigation and it is certain that only a small part of this decrease can be attributed to the above source.

Solutions of methyl iodide (this being one of the most volatile alkyl halides used) were used for a study of the question. Standard solutions were prepared by weighing into a measuring flask nearly full of absolute alcohol a slight excess over the calculated amount of methyl iodide. The volume of alcohol necessary to bring the solution to the desired strength was then added from a pipette, both solution and alcohol, of course, being at the correct temperature.

A normal solution of methyl iodide was prepared as above and two 10 cc. portions were withdrawn *by suction with an ordinary pipette.* Each of these was added to an aqueous solu-

tion of silver nitrate in a tube which was at once sealed and heated at 60° for 24 hours. The results of these analyses showed that about one per cent. of the alkyl halide had been lost in the process of making up and transferring the solutions.

These results were confirmed by other analyses, in some cases the loss of methyl iodide being even larger. It should be stated that the alkyl halide had been previously analyzed and was undoubtedly quite pure.

From these experiments it was realized that unless precautions were taken to eliminate the error involved by loss of alkyl halide, the velocity constants in long time-periods might be seriously affected. A special form of pipette has been therefore devised which has proved itself invaluable in working with the alkyl halides and volatile liquids and gases in general. Fig. I shows in detail the construction and mechanism of this apparatus, which is mounted on a suitable brass frame (*F*), and held in position by plaster of Paris in the small, raised, hollow, brass boxes (*S*).

The 10 cc. or 20 cc. pipette (*A*) is surrounded by a jacket (*B*) through which water from the constant temperature bath is made to circulate by a Brown and Sharp rotary pump. The solution to be measured out is contained in the flask (*R*), which, together with the wash-bulbs (*W*), is immersed in the constant temperature bath. A two-valve blowing bulb is attached at (*G*). The wash-bulbs (*W*) are filled with a small quantity of the solution to be measured out, in order that the air going through them may be saturated with the alcohol and alkyl halide, and hence not take up any from the solution in (*R*) and cause a decrease in the concentration of the alkyl halide solution contained therein. The bulbs (*C*) catch any solution that may be accidentally forced from (*A*). If a compressed air system is at hand the bulbs (*C*) can be half filled with mercury, which is then forced up and down by the air under pressure. In this way the same air is always kept in (*A*) and the left bulb (*C*) and is always saturated.

To fill the pipette, stopcock (*N*) is turned so as to connect (*A*) with (*R*), and the three-way stopcock (*M*) is turned so as to furnish an outlet from (*A*) to the air. On pressing the

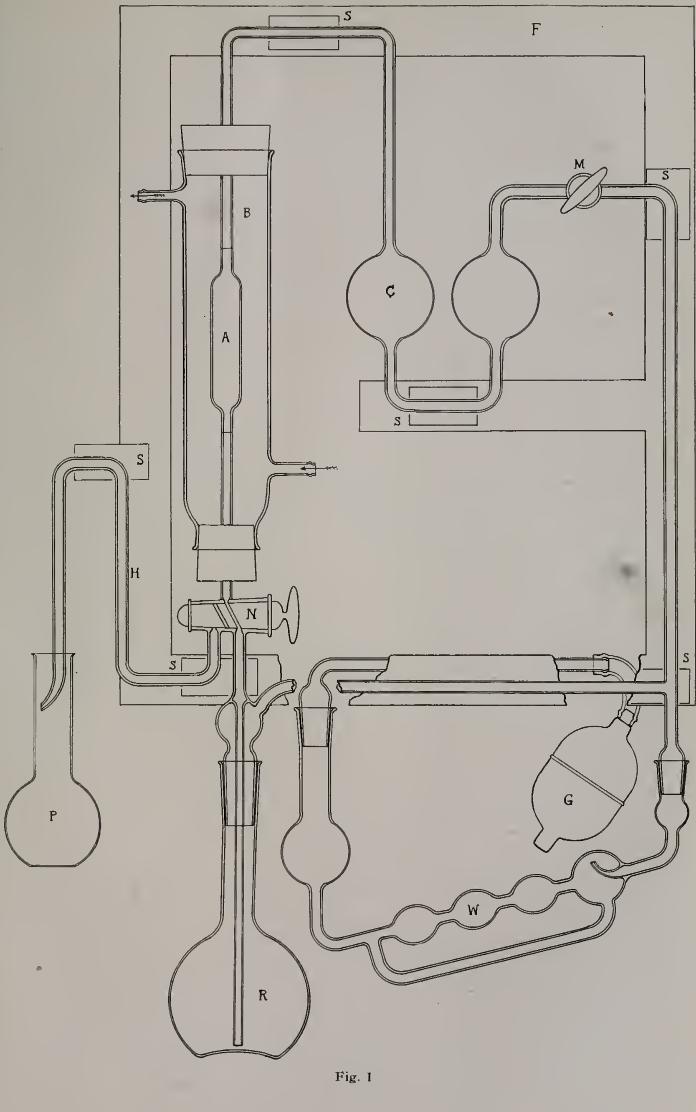


Fig. I

blowing bulb (*G*), the solution in (*R*) is forced into the pipette (*A*), the air which reaches the solution in (*R*) being saturated with the vapors of the alkyl halide and alcohol by passage through the wash-bulb (*W*). To deliver the pipette, stopcock (*M*) is turned so as to connect (*A*) with (*G*), (*W*) and (*R*). Stopcock (*N*) is turned so as to connect (*A*) with the capillary outflow tube (*H*). The liquid flows into the flask (*P*), the tip of the outflow tube (H) being held just under the surface of the sodium phenolate solution already in (*P*), and the pipette (*A*) is at the same time filled with the air which is already compressed in (*R*) and saturated with the vapor of the alkyl halide. The flasks (*P*) containing the sodium phenolate solutions are brought to the correct temperature in the bath before the alkyl halide solution is added, are kept at the right temperature in a beaker of water from the bath during the transfer of the alkyl halide, and are immediately closed with cork stoppers. The necks of the flasks are covered with "rubber fingers" to keep out water, and the flasks are then *shaken in the bath* to give the solutions perfect homogeneity and the correct temperature. When the capillary outflow tube (*H*) is well covered with binding tape or other insulating material there is no great difficulty in mixing the solutions at the desired temperature, 0°, 25° or 35°. This apparatus has been of great service in the work with alkyl iodides, solutions of ammonia, methylamine and other volatile substances. When it is used, the loss from volatilization is much less than is occasioned by the use of an ordinary pipette. We give the analyses which were made of three 10 cc. portions of methyl iodide measured out by the aid of the above device, many others having been made by Loy and Miss Brown. The alkyl halide solution was 0.3 per cent. stronger than normal.

Analyses	Percentage normal found	Percentage normal calculated
1	100.21	100.30
2	100.12	100.30
3	100.05	100.30

It is evident that the loss of methyl iodide involved when the apparatus described above is used is only 0.1 to 0.3 per

cent., which is much less than that incurred with the ordinary form of pipette, namely, about 1 per cent. Loy[1] has found that only about 0.1 per cent. of ethyl iodide is lost from N or 0.1 N solutions used in this apparatus. We have therefore always made the solutions of methyl iodide and ethyl bromide 0.3 per cent. too strong, and the solutions of ethyl iodide 0.1 per cent. too concentrated.

Experiments were carried out to determine whether alkyl halide is lost from the reaction flasks after they are stoppered and placed in the constant temperature baths. It was found that their weight did not decrease perceptibly even after standing a week. If alkyl halide escapes, we must assume that the same amount of water vapor enters through the stoppers, which is very improbable.

It is evident that the decrease in velocity constants noticed as the time-periods become longer cannot be attributed solely to loss of alkyl halide. At present it seems most probable that it is mainly due to a monomolecular side-reaction in which an olefin (or ether) is formed, because Brussoff[2] found that ethyl iodide and potassium hydroxide in ethyl alcohol at 78° give about 16 per cent. of the theoretical amount of ethylene. Since Brussoff did not exercise the very greatest care in freeing the olefins from the ethers formed simultaneously, we may consider this 16 per cent. a maximum amount at that temperature. There is certainly much less formed at lower temperatures; our own experiments show that there is a smaller decrease in the constants at 0° than at 25°. Furthermore, Johnson has carried out a large number of alkylations of the salts of urazoles at 60° in acetone, methyl alcohol and ethyl alcohol and has found evidence that the olefin formation is considerable, although not as much as 5 per cent. even when the reactions were 85 per cent. completed. In Johnson's work there was liberated one molecule of urazole acid for each molecule of olefin formed, according to the equation:

$$C_2H_5I + NaUr \longrightarrow C_2H_4 + NaI + UrH$$

and he was able to titrate this urazole acid with standard alkali,

[1] Loy: Dissertation, Johns Hopkins University, 1910.

[2] Z. physik. Chem., **34**, 129.

and hence calculate the amount of olefin formed. When this was done he was able to make a correction in his data and show that the velocity of the alkylation of the urazole salt was practically constant throughout. We cannot do this, however, in our work on the alkylation of phenolates and ethylates because the acids liberated, phenol and ethyl alcohol, are too weak to be titrated. We are therefore carrying out experiments to measure the amount of olefin formed, and shall then make the proper corrections in our data. We are, furthermore, studying the alkylations of the salts of urazoles and other fairly strong acids in absolute alcohol, and in this case we shall be able to study the amount of this side reaction by measuring the amount of urazole or other acid set free. We have evidence now that, notwithstanding the fact that added ether accelerates the reaction velocity, a small amount of the decrease in the velocity constant is due to the slight suppression of the ionization of the sodium phenolate by the sodium halide and ether formed in the reaction. The sodium phenolate and alkyl halides used, and the ethers and halide salts formed, change slightly the physical constants of the medium; the effects of solvation and viscosity on the ionic and molecular migration velocities, per cent. of ionization and reaction velocities will, therefore, be considered, but these effects seem to be counterbalanced in the present studies in such a way that the values for K_i and K_m are approximately the same for the concentrated as for the dilute solutions.

The amount of the decrease in the velocity constant is not over 3 to 5 per cent. even when the reaction is 75 per cent. complete, and in the first half of the reaction is hardly more than the unavoidable experimental errors. We have therefore disregarded this decrease in the present articles and shall leave the further study of this point to the last refinement of our researches along these lines.

Preparation[1] of Absolute Ethyl Alcohol

With the exception of a few series of reactions carried out to determine the effect of traces of water on reaction velocity,

[1] We have been aided in this work on alcohol by a grant from the C. M. Warren Fund.

the solvent used was invariably nearly absolute alcohol. The work of numerous investigators[1] has shown that the effect of water on the velocity of reactions of this type may be a very important factor, and one that must be considered if accurate measurements are to be made. While the effect of traces of water on reactions between sodium phenolate and alkyl halides is not so great as in some other cases, it is nevertheless quite appreciable, and it seemed advisable to eliminate this factor by the use of solvents as free from moisture as it was practicable to obtain them. The dehydration of ethyl alcohol is a comparatively simple matter. The best commercial article was boiled several days with 400 grams of calcium oxide per liter of alcohol. After distillation, the treatment with calcium oxide was repeated, using a smaller proportion than before. The last traces of moisture were often removed by digesting the alcohol with turnings of metallic calcium and calcium oxide at 40°. At this temperature the metal is only slowly acted upon by alcohol, and the dehydration is very effective. After the first portion of calcium has passed into solution, second and third portions of about 10 grams or less per liter may be added and allowed to react at a moderate temperature. Such treatment will always be found sufficient to produce alcohol of a high degree of dehydration. We have used calcium oxide and calcium simultaneously because we found that metallic calcium alone increases the specific gravity when boiled some time with the alcohol. The increase in specific gravity is probably due to a catalytic decomposition of the alcohol into water and ethylene (or ether), which escapes. A sample of alcohol which had increased in specific gravity an amount corresponding to 0.18 per cent. water when treated with calcium was boiled with calcium oxide and was then found to contain only 0.03 per cent. of water. Our best samples of alcohol have been obtained by the use of calcium oxide alone. We have found calcium carbide to be very effective in a short time. We shall report soon in another arti-

[1] Acree: This Journal, **41**, 457. Reid: *Ibid.*, **41**, 483. Goldschmidt and Sunde: Ber. d. chem. Ges., **39**, 711, and *loc. cit.* Joseph Gyr: *Ibid.*, **41**, 4322. Lapworth: J. Chem. Soc., **93**, 2163; *Loc. cit.* Bredig: *Loc. cit.* Biochem. *Z.*, **6**, 308. Ber. d. chem. Ges., **39**, 1756.

cle on some special apparatus and the methods found useful in preparing large quantities of pure alcohol.

Before the treatment with metallic calcium as above, the alcohol was invariably digested with 10 grams of silver nitrate or 3 grams of *m*-phenylenediamine hydrochloride per liter and distilled, after which it gave no decided tests for aldehydes.

It was found, in general, that the first treatment with calcium oxide gave alcohol of about 99.7 per cent. A second similar treatment in some cases gave alcohol of 99.99 per cent. purity. This was, however, only attained after several days' digestion at boiling temperature. It is much more convenient to remove the last traces of moisture with metallic calcium and calcium oxide.

It appears at present that specific gravity determinations made with a carefully calibrated pycnometer of at least 40 cc. capacity give the surest evidence of the dehydration of alcohol. The critical temperature of solution in kerosene, advocated by some investigators,[1] is hardly applicable as a test for absolute quantities of water, though it is certainly of great value in determining relative proportions. There is, necessarily, considerable variation, both in composition and dryness, between different samples of kerosene, and both factors are of essential importance. It was found that alcohol of specific gravity 0.78510 $\frac{25^\circ}{4^\circ}$, when mixed in equal volumes with a certain sample of commercial kerosene which had not been dried or distilled, gave a C. T. S. of 4°.02. With equal volumes of the same kerosene dried with calcium chloride and distilled the C. S. T. was —4°. Andrews suggests that kerosene used for this purpose be first treated by passing steam through it for a time to free it from its most volatiie constituents and then dried and used. We have found that the C. T. S. of alcohol in kerosene so treated will vary greatly with the length of time that steam is passed through the kerosene. As an extreme instance, kerosene treated in this way for two days, when dried and distilled, gave with (approximately) 100 per cent. alcohol a C. T. S. = 12°, while the portion of

[1] See L. W. Andrews: J. Am. Chem. Soc., **30**, 353.

the oil which was volatile with water vapor, when dried, showed no cloudiness when mixed with an equal volume of 100 per cent. alcohol at a temperature of —8°. It is evident that the low boiling constituents of kerosene give with alcohol a much lower C. T. S. than the high boiling constituents and consequently variations in composition of kerosene will give corresponding variations of critical solution temperature. To use this method as a criterion of dehydration of alcohol would be hardly safe until one had set a standard for his particular sample of kerosene. We have relied entirely on the specific gravity method, and have made comparison tests by the kerosene method.

The pycnometer[1] used for the determination of specific gravity was of the Ostwald-Sprengel type and had a capacity of approximately 50 cc. It was provided with close-fitting, ground glass caps to prevent evaporation during weighing. This pycnometer was carefully calibrated several times and its capacity was known with a probable error of 0.0002 cc. It seems that little is to be gained by the use of a pycnometer larger than this unless one has a balance which is exceptionally sensitive under a heavy load. After bringing the pycnometer and its contents to the temperature of the bath, it was adjusted, wiped dry and allowed to stand some time in the balance case, when its weight was taken. In all our later work a duplicate pycnometer filled with water, whose caps were sealed on permanently with Khotinski wax, was carried through all these operations simultaneously and used as a *tare* in weighing. In this way errors due to deposition of moisture on the glass from the air were obviated. It is still better to avoid the use of caps on the tare by fusing the ends of the capillary tubes.

A number of samples of alcohol were dehydrated as above and their specific gravities were determined. The following values have been obtained within the last few months. In each case the alcohol was treated with silver nitrate and with calcium oxide twice besides the further treatment with calcium turnings and calcium oxide:

[1] The details of measurements with these and other types of pycnometers will be given in a monograph on alcohol.

Sample (1)	Treated with four portions of metallic calcium, sp. gr. =	0.785072
Sample (2)	Treated with calcium three times, sp. gr. =	0.785093
Sample (3)	Dried with calcium three times, sp. gr. =	0.785088
Sample (4)	Dried with calcium three times, sp. gr. =	0.785088
Sample (5)	Dried with calcium three times, sp. gr. =	0.785088
Sample (6)	Dried with calcium three times, sp. gr. =	0.785088
Sample (7)	Dried with calcium four times (middle portion of distillate), sp. gr. =	0.785069
Sample (8)	Dried with calcium six times (middle portion of distillate), *lowest sp. gr.* =	0.785058

It seems that under ordinary conditions anhydrous alcohol, obtained by the action of quicklime and calcium turnings on the commercial article, has a specific gravity of about 0.785085. By very complete dehydration and by fractional distillation somewhat lower figures may be obtained.

From this work it seems that the most probable value[1] for the specific gravity of alcohol is 0.78506 $\frac{25^\circ}{4^\circ}$. It should be stated that the specific gravity of water at 25° used for the above calculations was 0.997077, the value obtained by Chappuis,[2] and that the temperatures are on the hydrogen scale. Work on the physical constants of alcohol will be continued in this laboratory.

Purification of Alkyl Halides

Ethyl Iodide.—For the preparation of pure ethyl iodide, the best obtainable iodine was added to red phosphorus in 100 per cent. alcohol, and the resulting compound was washed well

[1] This value 0.78506 is identical with the one obtained by McKelvey and Osborne, of the National Bureau of Standards, in their very fine investigation on the physical properties of ethyl alcohol. See Circular No. **19** of the Bureau of Standards: Standard Density and Volumetric Tables.

[2] Thiesen: Wiss. Abh. Phys.-Techn. Reichsanst., **3**, 68 (1900). Chappuis: Bur. Int. d. Poids Mesures, Trav. Mém., **13** (1907).

with dilute alkalies and water. After drying it for a few minutes with calcium chloride, the dehydration was completed with a small quantity of resublimed phosphorus pentoxide. The alkyl halide was distilled from this through a dry condenser and again allowed to stand over phosphorus pentoxide. The dried liquid was subsequently redistilled several times in dried apparatus and thus obtained in good condition. The effect of light on the decomposition of these compounds being very marked, containing vessels of brown glass were used. By the addition of a few drops of mercury ethyl iodide may be kept entirely colorless. That there is no appreciable interaction between the two was shown by boiling ethyl iodide, under a return condenser, for three days with one-fifth its volume of mercury. Even with this vigorous treatment the action is slight, for it was found that only a little mercurous iodide was formed. On distilling the alkyl halide, a trace of mercury was found in the distillate. It is probable that at the boiling temperature a little mercury ethyl is formed, but, at ordinary temperatures, the quantity is not appreciable.

The boiling point of ethyl iodide[1] prepared as above was found to be 72°.14–72°.17 under 760 mm.

Methyl Iodide.—The methyl alcohol used in the preparation of methyl iodide contained about 0.1 per cent. water. Only the best iodine was used. Phosphorus pentoxide was used as above to remove the last traces of water and alcohol. After drying and redistilling, the methyl iodide was kept in dark bottles over a little mercury.

Since very discordant values are given by different authorities[2] for the boiling point and specific gravity of methyl iodide, careful determinations of both values were made. The thermometer used for the boiling-point determination was graduated in tenths of a degree. This thermometer was subsequently checked against a standard platinum resistance thermometer. The following values[3] were obtained:

[1] Mr. Meserve obtained 72°.20, and Mr. Shrader 72°.19, as the boiling point of ethyl iodide under 760 mm. at about 22°.

[2] Dobriner: Ann. Chem. (Liebig), **243**, 23. Perkin: J. prakt. Chem., [2] **31**, 500.

[3] Miss Brown obtained 42°.35, 42°.35, 42°.35–38, and 42°.31–36, as the boiling point of methyl iodide under 760 mm. at about 22°.

Sample I. Dried with phosphorus pentoxide and redistilled four times. B. p. = 42°.32—42°.34 under 759.35 mm. pressure

Sample II. Dried as above and redistilled twice. B. p. = 42°.25—42°.31 under 757.65 mm. pressure

The specific gravity of Sample (II) was found to be 2.2619 $\frac{25°}{4°}$.

Analysis:

0.7978 gram methyl iodide gave 1.3200 gram silver iodide.

	Gram found	Gram calculated
I	0.7135	0.7133

A number of analyses have shown that these alkyl halides can easily be prepared in a state of great purity, the foreign substances amounting to perhaps 0.01 to 0.05 per cent. The details will be given by Miss Brown and Messrs. Shrader and Meserve.

Phenol

The phenol used was Kahlbaum's best. It was twice redistilled and boiled from 180°.1 to 180°.2, uncorrected. After distillation it was pulverized and dried in vacuum desiccators over concentrated sulphuric acid for several weeks. After this treatment, it is improbable that more than traces of water were present. In making up solutions with phenol, care was taken not to expose it to the air more than was necessary, since it is quite hygroscopic and we desired to exclude all water from the reagents. A small box containing the balance, desiccator, flasks, etc., and fitted with a glass window, arm holes and rubber gloves, and also containing a drying agent, such as calcium chloride, through which the enclosed air is circulated by means of a fan, is quite necessary in transferring hygroscopic substances from the desiccator to the weighing tubes and volumetric apparatus. The temperature can also be regulated very easily. The apparatus will be described in detail in another article by Mr. Meserve.

Standard Acids and Alkalies

Hydrochloric acid was used for all titrations. It was standardized in several ways, all of which agreed satisfactorily.

The method of Acree and Brunel[1] is convenient and gives very satisfactory results. Dry, gaseous hydrochloric acid was passed into a flask containing a weighed quantity of water, precautions being taken to prevent loss of water vapor. The amount of acid absorbed was determined directly by weight and the solution thus obtained used as a standard in making up a large quantity of normal acid. In our most accurate work *weighed portions* were analyzed to within 0.01–0.02 per cent. and the correct volume determined by accurate measurements of the specific gravity.

Standard hydrochloric acid was also prepared by Hulett's method[2] and the results obtained were quite satisfactory. The acids obtained by these two methods were found to check one another within 0.1 per cent. Two gravimetric analyses of hydrochloric acid by Hulett's method were made, one giving 99.97 per cent. of the calculated weight of silver chloride and the other 100.07 per cent.

Standard sodium hydroxide was made from the purest metallic sodium by the use of sodium amalgam, and also by dropping small pieces of the sodium on ice water. It was thought that this gave a somewhat sharper titration with methyl orange than was given by alkalies containing carbonate. The alkali was standardized by titrating it against standard hydrochloric acid and also by evaporating a known volume with an excess of pure hydrochloric acid and weighing the residue of sodium chloride after ignition. Methyl orange was invariably used in all titrations.

Temperature Regulation

Constant temperatures were maintained by the use of two baths, the one for work at 25° having a capacity of about 450 liters, and the other for work at 35° having a capacity of 40 liters. Both were provided with efficient stirrers and there was no difficulty in keeping their temperatures permanently constant to within 0°.01, which was entirely satisfactory for reaction and conductivity work.

In making specific gravity determinations, however,

[1] This Journal, **36**, 117.

[2] Hulett and Bonner: J. Am. Chem. Soc., **31**, 390.

it was necessary to read temperatures somewhat closer than 0°.01. A Beckmann thermometer was therefore compared carefully with the standard and kept in the bath constantly for use in this work. In the pycnometric determinations of alcohol the temperature was read to within several thousandths of a degree and was probably correct to within 0°.004.

The standard thermometers used in this work have been calibrated to about 0°.002 at the National Bureau of Standards, or at the Bureau de Poids et Mesures at Sèvres, and have been checked by Dr. B. B. Turner in this laboratory against a standard platinum resistance thermometer of the Dickinson-Mueller type[1] as used in the United States Bureau of Standards, and somewhat modified by Dr. Turner and Acree. Our temperature standard is accurate to about 0°.002, which is much closer than we can rely upon any ordinary mercury thermometer. We shall describe later a special cathetometer and telescope, and the auxiliary apparatus, with which we can easily read primary standard thermometers to 0°.001 and good burettes to 0.001 cc.

Conductivity Measurements

The cells were of several types which we have designed in this laboratory and which will be described in another paper.[2] They seem to have an advantage over the older types in that they are far more constant and less subject to abrupt changes under careless handling.

The bridge wire, resistance box, etc., were carefully calibrated. Three readings of each resistance were taken at different points on the bridge wire and the results averaged, the mean values for the ionization μ_v/μ_∞ being given in Table XII. All conductivities are expressed in reciprocal ohms. The values used for μ_∞ were obtained by the direct measurement of the resistance of the N/2048, N/8096 and N/16182 solutions, which are practically completely ionized.

We have suspected for some time[3] that the differences in

[1] Bull. U. S. Bur. Standards., Vol. **3**, No. 4.

[2] Robertson and Acree: Address before the Int. Cong. Applied Chem., New York, September, 1912.

[3] Shadinger and Acree: This Journal, **39**, 231; **44**, ——, and later papers.

the viscosity of the different solutions will be found to have an influence on the velocity of movement of the different substances in solution and hence alter the reaction velocities in certain cases, and change the apparent per cent. of ionization of the various salts in the solution. If the ions of sodium ethylate move more slowly in the more viscous normal solutions than they do in the 0.1 N solutions, the conductivity measurements will not give us a true measure of the per cent. of ionization in the two cases. We should be compelled, therefore, to make a correction for the viscosity of the more concentrated solutions. No method is known at present, however, for doing this with certainty. One of us wrote of this problem to Professor A. A. Noyes, who at once kindly sent us two pages of a manuscript which he has since published.[1] Noyes' method is to multiply the apparent per cent. of ionization of the salt in a given solution by the ratio of the viscosity of this solution to that of the pure solvent. We have made measurements of the viscosities of various solutions of sodium ethylate, sodium phenolate, sodium iodide, and various mixtures of these, in absolute ethyl alcohol at 25° and 35°. The relation of the viscosities and conductivities of N, 0.5 N, and 0.25 N solutions of sodium phenolate and sodium ethylate, for example, are such that if we were to apply Noyes' method we should arrive at the conclusion that the per cent. of ionization is the same for the N, 0.5 N and 0.25 N solutions. Such a conclusion is, however, not in harmony with all the known facts of physical chemistry and certainly not borne out by our experimental results. We have thought of using some formula such as the expression $\alpha\sqrt{\frac{V_N}{V_o}}$ in which V_o and V_N are the viscosities of the pure solvent and of the solution studied. Until further work can be done by the use of *other methods* to give us a direct measure of the real ionic velocities we do not see any clear way to solve this problem. We are at present trying to measure the conductivities, the viscosities by Bingham's methods and the migration velocities and solvation by Washburn's methods in order to learn the true per cent. of ionization of our com-

[1] Noyes and Lombard: J. Am. Chem. Soc., **33**, 1424. Washburn: *Ibid.*, **33**, 1464.

pounds. We have tried to apply Noyes' correction, as well as our own, in determining whether the formula $K_N = K_i\alpha + K_m \frac{(\alpha)^2}{V}$ gives us constants for K_i and K_m when such correction is made (see page 480). The results have not been at all satisfactory. The best plan is to work with solutions which are so dilute that the viscosities are all practically the same as that of the pure solvent. It can be seen how great the difficulty is in making such a correction when it is realized that the viscosity of a N solution of sodium phenolate or sodium ethylate is nearly three times as large as that of the pure ethyl alcohol, and that the viscosity of our reaction mixtures is constantly changing. We have therefore extended our studies to regions as dilute as can possibly be measured with reasonable accuracy. It is a peculiar fact that our constants for K_i and K_m are practically the same for N solutions as for the dilute solutions, and we may find on further work that the "viscosity effects" influence the reaction velocities and the conductivities in such a way as to annul the errors discussed above. This field is a bright one for investigation. It is very fortunate for others who work with aqueous solutions that the viscosity of their most concentrated solutions is not greatly different from that of water; the errors cannot be very great in any case. We are measuring the viscosities of all of our solutions before and after the reactions are complete, and even during the reactions, to collect data which may shed light on this problem. We have also measured the change in volume in a number of cases, and have attempted to use the dilatometer in some cases to follow the velocity of the reaction. If the solution changes in volume there will be a corresponding change in the concentrations, for which we must make corrections. Certain energy changes will also be involved in the change of volume and these may be of great interest in the future. As we have pointed out before, chemists should consider in these studies every possible chemical and physical factor.

see errat
p. 548.

Measurements and Calculations of Reaction Velocities

The reactions were interrupted at the end of the desired

time-period by removing the small flask from the bath and pouring its contents into 200 cc. of cold distilled water, after which the titration with standard 0.2 N or 0.1 N hydrochloric acid was immediately made, and the amount of unchanged sodium phenolate thus determined. It was found by experiment that the above procedure involved no appreciable error, the progress of the reaction being practically reduced to zero by dilution with the large volume of cold water.

In the tables which follow, the constants have been calculated from the equations:

$$(1)\quad K_N/V = K_V = \frac{1}{t}\cdot\frac{x}{A-x} \text{ (for equivalent masses)}$$

and

$$(2)\quad K_N/V = K_V = \frac{B}{t(B-A)}\log n\frac{B(A-x)}{A(B-x)} \text{ (for unequal masses)}$$[1]

In this way both sets of velocity constants are referred to the same basis and become comparable.

The values given for A generally represent the actual volumes in cc. of the sodium phenolate solutions used. Under x is given the number of cc. of standard acid required for each titration, *referred to the same normality as the sodium phenolate solution used in that particular series of reactions.* These values of x therefore actually represent the volumes of A that have disappeared at the end of each time-period. K_N represents the velocity constant for each series when referred to the normal basis. It is obtained by multiplying the constant K_V by the dilution, V, in liters, of the sodium phenolate after mixture with the alkyl halide solution.

Summary

Tables I to XI and XIII and XIV illustrate the decrease in velocity of the reaction as increasing excesses of phenol are added. The general relations are shown in Table XI.

In Table XII we give the approximate ionization of sodium phenolate at 25° and 35° in solutions varying from N/1 to N/32. These have not yet been corrected for the influence of viscosity and solvation.

[1] Hecht, Conrad and Brückner: Z. physik. Chem., 3, 455.

Tables XIII to XXIV show the velocities of the reactions of sodium phenolate and methyl iodide at 25° in solutions varying from N/1 to N/32. Table XXV gives the average values for K_N, Table XXVI gives the values for K_i and K_m, and Table XXVII gives the values for "K_N found," "K_N calculated," and the experimental errors.

Tables XXVIII to XXXVIII give the velocity of transformation of sodium phenolate and methyl iodide at 35° in solutions varying from N/2 to N/40. Table XXXIX gives the average values for K_N, Table XL gives the values for K_i and K_m and Table XLI gives the values of "K_N found," "K_N calculated" and the experimental errors.

Tables XLII to LI give the reaction velocities for sodium phenolate and ethyl iodide at 25° in solutions varying from N/1 to N/16. Table LII gives the average values for K_N, Table LIII gives the values for K_i and K_m, and Table LIV gives the values "K_N found," "K_N calculated," and the experimental errors.

Tables LV to LXII give the reaction velocities for sodium phenolate and ethyl iodide at 35° in concentrations varying from N/2 to N/16. Table LXIII gives the average values of K_N, Table LXIV gives the values of K_i and K_m and Table LXV gives the values for "K_N found," "K_N calculated," and the experimental errors.

Table LXVI gives a résumé of all the values for K_i and K_m.

THE EFFECT OF AN EXCESS OF PHENOL ON THE REACTION VELOCITY AT 25°

Table I—0.5 N Sodium Phenolate and 0.25 N Methyl Iodide (no Excess Phenol) at 25°

$A = 10.02$

t	x	K_V
30	1.28	0.00488
40	1.62	0.00482
50	1.90	0.00468
60	2.16	0.00458
80	2.66	0.00452
100	3.09	0.00446

Average K_V = 0.00466

Table II—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (no Excess Phenol) at 25°

$A = 10.00$

t	x	K_V
40	1.62	0.00483
50	1.95	0.00484
60	2.17	0.00462
80	2.70	0.00462
100	3.14	0.00458
140	3.86	0.00449

Average K_V = 0.00466

For Reactions with 1 per cent. Excess Phenol, see Tables XII and XIII.

Table III—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (2 per cent. Excess Phenol) at 25°

$A = 10.00$

t	x	K_V
30	1.22	0.00463
40	1.54	0.00455
50	1.88	0.00463
65	2.31	0.00462
75	2.54	0.00454
90	2.84	0.00441

Average K_V = 0.00456

Table IV—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (2 per cent. Excess Phenol) at 25°

$A = 10.00$

t	x	K_V
30	1.20	0.00454
40	1.53	0.00451
50	1.86	0.00457
60	2.14	0.00454
70	2.44	0.00460
100	3.09	0.00447

Average K_V = 0.00454

Table V—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (5 per cent. Excess Phenol) at 25°

$A = 10.04$

t	x	K_V
30	1.15	0.00431
40	1.47	0.00428
50	1.77	0.00428
60	2.06	0.00430
70	2.32	0.00429
90	2.99	0.00428

Average K_V = 0.00429

Table VI—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (5 per cent. Excess Phenol) at 25°

$A = 10.01$

t	x	K_V
30	1.16	0.00436
40	1.48	0.00434
50	1.79	0.00435
60	2.06	0.00432
100	3.04	0.00436

Average K_V = 0.00435

Table VII—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (10 per cent. Excess Phenol) at 25°

$A = 10.04$

t	x	K_V
20	0.76	0.00409
30	1.12	0.00418
40	1.42	0.00412
50	1.73	0.00416
60	1.98	0.00409
80	2.48	0.00410

Average K_V = 0.00412

Table VIII—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (10 per cent. Excess Phenol) at 25°

$A = 10.05$

t	x	K_V
20	0.754	0.00406
30	1.106	0.00412
40	1.44	0.00418
50	1.69	0.00404
60	1.97	0.00406

Average K_V = 0.00409

Table IX—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (20 per cent. Excess Phenol) at 25°

$A = 10.01$

t	x	K_V
20	0.71	0.00382
40	1.34	0.00386
50	1.65	0.00395
60	1.90	0.00390
90	2.62	0.00395
260	5.05	0.00391

Average K_V = 0.00390

Table X—0.5N Sodium Phenolate and 0.5 N Methyl Iodide (30 per cent. Excess Phenol) at 24°.95

$A = 10.01$

t	x	K_V
30	0.99	0.00365
40	1.28	0.00367
50	1.57	0.00372
60	1.80	0.00365
80	2.27	0.00366
100	2.69	0.00367
123	3.10	0.00365

Average K_V = 0.00367

Table XI—Resume of the Reaction Velocities for 0.5 N Sodium Phenolate, 0.5 N Methyl Iodide and an Excess of Phenol at 25°

Excess of phenol in per cent.	K_V	K_V calculated
0	0.00466	0.00467
1	0.00462	0.00463
2	0.00455	0.00460
5	0.00432	0.00450
10	0.00410	0.00432
20	0.00390	0.00397
30	0.00367	0.00362

Table XII—The Ionization of Sodium Phenolate at 25° and 35°

Ionization at 25°

V	α	$1-\alpha$
1	0.122	0.878
2	0.189	0.811
4	0.258	0.742
8	0.335	0.665
16	0.419	0.581
32	0.509	0.491

Ionization at 35°

V	α	$1-\alpha$
2	0.185	0.815
4	0.247	0.753
8	0.319	0.681
16	0.399	0.601
32	0.486	0.514
40	0.516	0.484

REACTIONS BETWEEN SODIUM PHENOLATE AND METHYL IODIDE AT 25°

Table XIII—1 N Sodium Phenolate and 1 N Methyl Iodide at 25°

$A = 10.00$

t	x	K_V
20	1.33	0.00780
30	1.87	0.00766
40	2.35	0.00767
50	2.78	0.00770
60	3.14	0.00762
80	3.75	0.00750

Average K_V = 0.00766
K_N = 0.00766

Table XIV—1 N Sodium Phenolate and 1 N Methyl Iodide at 25°

$A = 10.00$

t	x	K_V
20	1.34	0.00773
30	1.87	0.00766
40	2.34	0.00764
50	2.74	0.00755
60	3.11	0.00752

Average K_V = 0.00762
K_N = 0.00762

Table XV—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 25°

$A = 10.00$

t	x	K_V
30	1.24	0.00471
40	1.56	0.00462
51	1.91	0.00462
60	2.18	0.00464
70	2.45	0.00464
80	2.66	0.00452
100	3.14	0.00457

Average K_V = 0.00462
K_N = 0.00924

Table XVI—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 25°

$A = 9.98$

t	x	K_V
21	0.91	0.00478
30	1.22	0.00464
40	1.56	0.00463
50	1.88	0.00465
60	2.16	0.00460
80	2.65	0.00452
120	3.52	0.00454

Average K_V = 0.00462
K_N = 0.00924

Table XVII—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 10.00$

t	x	K_V
30	0.736	0.00265
40	0.98	0.00271
50	1.18	0.00267
60	1.39	0.00269
70	1.56	0.00264
82	1.77	0.00262
150	2.80	0.00259

Average K_V = 0.00265
K_N = 0.01060

Table XVIII—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 10.00$

t	x	K_V
50	1.20	0.00273
60	1.41	0.00274
70	1.59	0.00270
90	1.92	0.00265
100	2.12	0.00269
110	2.29	0.00269

Average K_V = 0.00270
K_N = 0.01080

Table XIX—0.125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 10.00$ $B = 20.00$

t	x	K_V
40	1.18	0.00162
54	1.52	0.00159
65	1.78	0.00158
75	1.99	0.00156
85	2.22	0.00157
100	2.52	0.00156

Average $K_V = 0.00158$
$K_N = 0.01264$

Table XX—0.125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 10.00$ $B = 20.00$

t	x	K_V
40	1.20	0.00165
50	1.44	0.00161
60	1.66	0.00158
70	1.91	0.00159
80	2.14	0.00160
100	2.56	0.00158

Average $K_V = 0.00160$
$K_N = 0.01280$

Table XXI—0.0625 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 10.00$ $B = 40.00$

t	x	K_V
40	1.32	0.000900
50	1.66	0.000928
60	1.90	0.000900
70	2.20	0.000914
80	2.42	0.000894

Average $K_V = 0.000907$
$K_N = 0.01451$

Table XXII—0.0625 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 20.00$ $B = 80.00$

t	x	K_V
50	3.27	0.000912
60	3.84	0.000911
70	4.34	0.000909
80	4.87	0.000901
90	5.33	0.000893
100	5.79	0.000889

Average $K_V = 0.000902$
$K_N = 0.01443$

Table XXIII—0.03125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 20.00$ $B = 160.00$

t	x	K_V
70	5.06	0.000529
80	5.63	0.000525
90	6.24	0.000529
100	6.69	0.000520
110	7.20	0.000520
120	7.67	0.000517

Average $K_V = 0.000523$
$K_N = 0.01674$

Table XXIV—0.03125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 20.00$ $B = 160.00$

t	x	K_V
60	4.51	0.000539
70	5.03	0.000525
80	5.60	0.000523
90	6.16	0.000522
100	6.69	0.000520

Average $K_V = 0.000526$
$K_N = 0.01683$

Table XXV—K_N Found for Sodium Phenolate and Methyl Iodide at 25°

Conc. $NaOC_6H_5$ V	K_N	Average K_N
1	0.00766	
	0.00762	0.00764
2	0.00924	
	0.00924	0.00924
4	0.01060	
	0.01080	0.01070
8	0.01264	
	0.01280	0.01272
16	0.01451	
	0.01443	0.01447
32	0.01674	
	0.01683	0.01678

Table XXVI—K_i and K_m Found for Sodium Phenolate and Methyl Iodide at 25°

	K_i	K_m
$V = 1 : V = 2$	0.0286	0.00473
$V = 1 : V = 4$	0.0274†	0.00489†
$V = 1 : V = 8$	0.0286*	0.00473*
$V = 1 : V = 16$	0.0278*	0.00483*
$V = 1 : V = 32$	0.0283*	0.00476*
$V = 2 : V = 4$	0.0264	0.00524
$V = 2 : V = 8$	0.0286†	0.00473†
$V = 2 : V = 16$	0.0276*	0.00494*
$V = 2 : V = 32$	0.0283*	0.00478*
$V = 4 : V = 8$	0.0300	0.00393
$V = 4 : V = 16$	0.0281†	0.00466†
$V = 4 : V = 32$	0.0286*	0.00445*
$V = 8 : V = 16$	0.0266	0.00574
$V = 8 : V = 32$	0.0282†	0.00490†
$V = 16 : V = 32$	0.0294	0.00372
Average	0.0282	0.00474
Average[1]	0.02815	0.00477
Average[2]	0.0282	0.00475

[1] The average of all the values with daggers and asterisks.
[2] The average of all the values with asterisks.

Table XXVII—K_N Calculated and Found for Sodium Phenolate and Methyl Iodide at 25°

V	α	$1-\alpha$	K_N found	K_N calculated	Error in per cent.
1	0.122	0.878	0.00764	0.00760	+0.5
2	0.189	0.811	0.00924	0.00917	+0.8
4	0.258	0.742	0.01070	0.01079	—0.8
8	0.335	0.665	0.01272	0.01260	+1.0
16	0.419	0.581	0.01447	0.01457	—0.7
32	0.509	0.491	0.01678	0.01668	+0.6

REACTIONS BETWEEN SODIUM PHENOLATE AND METHYL IODIDE AT 35°

Table XXVIII—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 35°

$A = 9.98$

t	x	K_V
20	2.18	0.01397
30	2.93	0.01385
40	3.55	0.01381
50	4.08	0.01383
60	4.50	0.01368

Average K_V = 0.01383
K_N = 0.02766

Table XXIX—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 35°

$A = 10.00$

t	x	K_V
30	2.98	0.01412
40	3.60	0.01406
50	4.13	0.01407
60	4.53	0.01381
72	4.96	0.01367
85	5.42	0.01392

Average K_V = 0.01394
K_N = 0.02788

Table XXX—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 9.98$

t	x	K_V
40	2.44	0.00808
50	2.86	0.00808
60	3.21	0.00791
70	3.59	0.00802
100	3.89	0.00798
	4.39	0.00785

Average K_V = 0.00798
K_N = 0.03192

Table XXXI—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 10.00$

t	x	K_V
30	1.94	0.00802
40	2.43	0.00802
50	2.84	0.00793
60	3.23	0.00795
70	3.58	0.00795
80	3.89	0.00793

Average K_V = 0.00797
K_N = 0.03188

Table XXXII—0.125 N Sodium Phenolate and 0.125 N Methyl Iodide at 35°

$A = 10.00$

t	x	K_V
50	1.98	0.00493
60	2.24	0.00481
70	2.52	0.00481
80	2.77	0.00482
90	2.98	0.00472

Average $K_V = 0.00482$
$K_N = 0.03856$

Table XXXIII—0.125 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 10.00$ $B = 20.00$

t	x	K_V
20	1.66	0.00474
30	2.42	0.00492
40	3.02	0.00490
50	3.52	0.00481
60	3.95	0.00472
70	4.39	0.00472

Average $K_V = 0.00480$
$K_N = 0.03840$

Table XXXIV—0.0625 N Sodium Phenolate and 0.125 N Methyl Iodide at 35°

$A = 20.00$ $B = 40.00$

t	x	K_V
75	6.34	0.00278
80	6.72	0.00282
90	7.30	0.00281
100	7.84	0.00279
110	8.24	0.00281

Average $K_V = 0.00280$
$K_N = 0.04480$

Table XXXV—0.0625 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 10.00$ $B = 39.904$

t	x	K_V
45	3.815	0.00281
55	4.373	0.00279
65	4.821	0.00272
75	5.331	0.00276
85	5.674	0.00269
95	6.010	0.00266

Average $K_V = 0.00274$
$K_N = 0.0444$

Table XXXVI — 0.03125 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 20.00$ $B = 160.00$

t	x	K_V
60	10.37	0.00158
70	11.36	0.00156
80	12.35	0.00157
90	13.32	0.00160

Average $K_V = 0.00158$
$K_N = 0.05056$

Table XXXVII—0.03125 N Sodium Phenolate and 0.125 N Methyl Iodide at 35°

$A = 20.00$ $B = 80.00$

t	x	K_V
60	6.37	0.00167
70	7.04	0.00163
80	7.78	0.00162
100	8.96	0.00159
110	9.60	0.00159

Average $K_V = 0.00162$
$K_N = 0.0518$

Table XXXVIII — 0.025 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 40.00 \quad B = 400.00$

t	x	K_V
45	17.96	0.00136
75	24.60	0.00132
90	27.50	0.00134
110	29.80	0.00130

Average $K_V = 0.00133$
$K_N = 0.0532$

Table XXXIX—K_N Found for Sodium Phenolate and Methyl Iodide at 35°

Conc. $NaOC_6H_5$ V	K_N	Average K_N
2	0.02766 0.02788	0.02777
4	0.03192 0.03188	0.03190
8	0.03856 0.03840	0.03843
16	0.04480 0.04440	0.04460
32	0.05056 0.05180	0.05120
40	0.05320	0.05320

Table XL—K_i and K_m Found for Sodium Phenolate and Methyl Iodide at 35°

	K_i	K_m
$V = 2 : V = 4$	0.082	0.0155
$V = 2 : V = 8$	0.093	0.0130
$V = 2 : V = 16$	0.092	0.0133
$V = 2 : V = 32$	0.093	0.0134
$V = 4 : V = 8$	0.101	0.0093
$V = 4 : V = 16$	0.095	0.0113
$V = 4 : V = 32$	0.092	0.0120
$V = 8 : V = 16$	0.090	0.0141
$V = 8 : V = 32$	0.090	0.0143
$V = 16 : V = 32$	0.090	0.0143
$V = 2 : V = 40$	0.090	0.0136
$V = 4 : V = 40$	0.091	0.0123
$V = 8 : V = 40$	0.089	0.0144
Average	0.091	0.0131

Table XLI—K_N Calculated and Found for Sodium Phenolate and Methyl Iodide at 35°

V	K_N Found	K_N Calculated	Error in per cent.
2	0.0278	0.0275	+1.1
4	0.0319	0.0323	—1.2
8	0.0385	0.0379	+1.6
16	0.0448	0.0442	+0.9
32	0.0506	0.0509	+0.6
40	0.0532	0.0533	—0.2

REACTIONS BETWEEN SODIUM PHENOLATE AND ETHYL IODIDE AT 25°

Table XLII—1 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 9.96$

t	x	K_V
50	0.712	0.00154
60	0.86	0.00157
80	1.09	0.00153
95	1.285	0.00158
120	1.54	0.00153

Average K_V = 0.00155
K_N = 0.00155

Table XLIII—1 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 10.00$

t	x	K_V
30	0.455	0.001554
43	0.626	0.001552
57	0.830	0.001584
68	0.954	0.001551
79	1.090	0.001548
90	1.226	0.001553

Average K_V = 0.001557
K_N = 0.001557

Table XLIV—0.5 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 10.00$ $B = 20.00$

t	x	K_V
30	0.54	0.000937
50	0.86	0.000919
60	1.01	0.000912
70	1.19	0.000932
80	1.34	0.000932

Average K_V = 0.000926
K_N = 0.001852

Table XLV—0.5 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$

t	x	K_V
60	0.530	0.000930
70	0.610	0.000928
80	0.710	0.000955
90	0.770	0.000927
100	0.836	0.000912
110	0.908	0.000908

Average K_V = 0.000927
K_N = 0.001854

Table XLVI—0.25 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 9.98$ $B = 39.92$

t	x	K_V
30	0.65	0.000566
45	0.96	0.000568
60	1.186	0.000534
70	1.33	0.000518
90	1.70	0.000529
115	2.18	0.000550

Average $K_V = 0.000544$
$K_N = 0.002176$

Table XLVII—0.25 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$ $B = 20.00$

t	x	K_V
70	0.71	0.000527
80	0.80	0.000532
90	0.91	0.000543
100	0.99	0.000535
110	1.11	0.000550
120	1.20	0.000550

Average $K_V = 0.000546$
$K_N = 0.002184$

Table XLVIII—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$ $B = 40.00$

t	x	K_V
60	0.71	(0.000309)
70	0.85	0.000320
80	0.95	0.000316
90	1.06	0.000316
100	1.18	0.000318
110	1.27	0.000313

$K_V = 0.0003166$
$K_N = 0.002533$

Table XLIX—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 20.00$ $B = 80.00$

t	x	K_V
60	1.44	0.000322
70	1.68	0.000317
80	1.91	0.000317
90	2.14	0.000319
100	2.35	0.000317
110	2.54	0.000315

Average $K_V = 0.000318$
$K_N = 0.002544$

Table L—0.0625 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$ $B = 80.00$

t	x	K_V
61	0.84	0.000181
75	1.04	0.000184
90	1.25	0.000187
105	1.42	0.000184
120	1.58	0.000180
140	1.80	0.000179

Average $K_V = 0.000182$
$K_N = 0.00292$

Table LI—0.0625 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 20.00$ $B = 160.00$

t	x	K_V
60	1.68	0.000184
70	1.91	0.000181
80	2.15	0.000180
90	2.40	0.000179
100	2.64	0.000178

Average $K_V = 0.0001804$
$K_N = 0.00289$

Table LII—K_N Found for Sodium Phenolate and Ethyl Iodide at 25°

V	K_N	Average K_N
1	0.00155 0.00156	0.00155
2	0.00185 0.00185	0.00185
4	0.00216 0.00218	0.00217
8	0.00254 0.00254	0.00254
16	0.00289 0.00292	0.00290

Table LIII—K_i and K_m Found for Sodium Phenolate and Ethyl Iodide at 25°

	K_i	K_m
$V = 1 : V = 2$	0.0055	0.00100
$V = 1 : V = 4$	0.0056	0.00099
$V = 1 : V = 8$	0.0056	0.00098
$V = 1 : V = 16$	0.0058	0.00099
$V = 2 : V = 4$	0.0056	0.00097
$V = 2 : V = 8$	0.0057	0.00096
$V = 2 : V = 16$	0.0056	0.00099
$V = 4 : V = 8$	0.0054	0.00093
$V = 4 : V = 16$	0.0055	0.00100
$V = 8 : V = 16$	0.0054	0.00110
Average	0.0056	0.00099

Table LIV—K_N Found and Calculated for Sodium Phenolate and Ethyl Iodide at 25°

V	K_N Found	K_N Calculated	Error in per cent.
1	0.00155	0.00155	0.00
2	0.00185	0.00186	—0.50
4	0.00217	0.00218	—0.50
8	0.00254	0.00253	+0.40
16	0.00290	0.00292	—0.60

REACTIONS BETWEEN SODIUM PHENOLATE AND ETHYL IODIDE AT 35°

Table LV — 0.5 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°

$A = 9.98$

t	x	K_V
40	1.09	0.00306
50	1.32	0.00305
60	1.53	0.00302
70	1.74	0.00302
80	1.98	0.00299

Average $K_V = 0.00303$
$K_N = 0.00606$

Table LVI—0.5 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°

$A = 9.97$

t	x	K_V
40	1.09	0.00307
50	1.30	0.00300
60	1.54	0.00304
70	1.73	0.00300
80	1.92	0.00298

Average $K_V = 0.00302$
$K_N = 0.00604$

Table LVII—0.25 N Sodium Phenolate and 0.25 N Ethyl Iodide at 35°

$A = 19.94$

t	x	KV
40	1.33	0.00178
50	1.60	0.00175
60	1.88	0.00174
70	2.17	0.00174
80	2.46	0.00176

Average $K_V = 0.00176$
$K_N = 0.00704$

Table LVIII—0.25 N Sodium Phenolate and 0.50 N Ethyl Iodide at 34°.9[1]

$A = 10.00$ $B = 19.96$

t	x	K_V
40	1.25	0.001728
50	1.54	0.001746
60	1.82	0.001762
70	2.08	0.001766
80	2.28	0.001725
90	2.48	0.001700

Average $K_V = 0.001738$
$K_N\ (34°.9) = 0.006952$
$K_N\ (35°.0) = 0.00701$

Table LIX—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°

$A = 20.00$ $B = 80.00$

t	x	K_V
40	2.92	0.001006
60	4.14	0.000993
80	5.26	0.000988
100	6.36	0.000999
120	7.28	0.000993
140	8.20	0.000999

Average $K_V = 0.000996$
$K_N = 0.00797$

Table LX—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°.1

$A = 10.00$ $B = 40.00$

t	x	K_V
50	1.82	0.001029
60	2.12	0.001021
75	2.56	0.001020
80	2.66	0.001002
90	3.00	0.001032

Average $K_V = 0.001021$
$K_N(35°.1) = 0.00817$
$K_N(35°) = 0.00807$

[1] In these experiments the temperature of the bath was 34°.9. We have therefore used the equation $K_T = K_{T_0} \times 10^{(0.0526\,T - 0.0526\,T_0)}$ (Hecht and Conrad: Z. physik. Chem., **3**, 465) to correct for 35°.0.

Table LXI—0.0625 N Sodium Phenolate and 0.25 N Ethyl Iodide at 35°

$A = 20.00$ $B = 80.00$

t	x	K_V
40	1.78	0.000589
50	2.16	0.000579
60	2.58	0.000585
70	3.02	0.000587
80	3.31	0.000578

Average K_V = 0.000584
K_N = 0.00934

Table LXII—0.0625 N Sodium Phenolate and 0.25 N Ethyl Iodide at 35°.1

$A = 20.00$ $B = 80.00$

t	x	K_V
50	2.20	0.000592
60	2.58	0.000585
70	3.04	0.000600
80	3.39	0.000593
90	3.67	0.000577

Average K_V = 0.000590
$K_N(35°.1)$ = 0.00944
$K_N(35°)$ = 0.00933

Table LXIII—K_N Found for Sodium Phenolate and Ethyl Iodide at 35°

Conc. $NaOC_6H_5$ V	K_N	Average K_N
2	0.00604 0.00606	0.00605
4	0.00704 0.00701[1]	0.00702
8	0.00807[1] 0.00797	0.00802
16	0.00934 0.00933[1]	0.00933

Table LXIV—K_i and K_m Found for Sodium Phenolate and Ethyl Iodide at 35°

	K_i	K_m
$V = 2 : V = 4$	0.0188	0.00315
$V = 2 : V = 8$	0.0181	0.00333
$V = 2 : V = 16$	0.0185	0.00321
$V = 4 : V = 8$	0.0175	0.00359
$V = 4 : V = 16$	0.0185	0.00327
$V = 8 : V = 16$	0.0191	0.00280
Average	0.0184	0.00323

[1] These constants were calculated for 35° from the data obtained experimentally at 34°.9 and 35°.1.

Table LXV—K_N Calculated and Found for Sodium Phenolate and Ethyl Iodide at 35°

V	K_N Found	K_N Calculated	Error in per cent.
2	0.00605	0.00604	+0.2
4	0.00702	0.00698	+0.6
8	0.00802	0.00806	—0.5
16	0.00933	0.00928	+0.5

Table LXVI—Resume of All the Values for K_i and K_m

	K_i	K_m
Sodium phenolate and methyl iodide at 25°.	0.0282	0.00474
Sodium phenolate and methyl iodide at 35°	0.091	0.0131
Sodium phenolate and ethyl iodide at 25°	0.0056	0.00099
Sodium phenolate and ethyl iodide at 35°	0.0184	0.00323

CONCLUSIONS

1. In this article we have shown that the theory that only the ionized portions of electrolytes are chemically active is only partially correct, and that much of the earlier work on which this theory was based was interpreted unfortunately. We should therefore consider the possibility that both the ions and the nonionized forms of electrolytes may undergo transformation with comparable velocities, which may be influenced by so-called "salt effects" and other physical factors. With this theory in mind, the work presented here was undertaken.

2. A full description of the apparatus and quantitative methods is given in the experimental portion.

3. A list of tables is given in which we present the velocities of the reactions of sodium phenolate with methyl iodide and with ethyl iodide at 25° and 35° in absolute ethyl alcohol, the concentrations varying from N/1 to N/40.

4. The proper numerical data are substituted in a general formula, $K_N = K_i\alpha + K_m(1 - \alpha)$, and the series of simultaneous equations so obtained are solved. Constant values are obtained for K_i and K_m, which represent the velocity of

transformation of unit concentrations of phenolate ions, nonionized sodium phenolate and alkyl halides. We have interpreted this fact as evidence that both the phenolate ions and the nonionized sodium phenolate react with the nonionized alkyl halides, although we wish to point out that there may be an "abnormal salt effect" not yet understood.

5. If this theory is correct, the same value should be obtained for K_i, the velocity of transformation of unit concentrations of the phenolate ions and a given alkyl halide, whether the source of the phenolate ions be the sodium, potassium, lithium or other salts. The work reported here and other studies by Mr. Shrader, which are touched on now and will be reported in detail later, are discussed on pages 483 and 484, and it is shown there that the same alkyl halide actually does give practically the same value for K_i for sodium, potassium and lithium phenolates.

6. We suspect that the values for K_i and K_m given here may involve an "abnormal salt effect," which we shall next try to determine by measuring the reaction velocities in solutions varying from N/1 to N/2048, if possible. A similar study has already been made by Dr. C. N. Myers, who has shown that *p*-bromobenzonitrile and sodium, potassium and lithium ethylates, in solutions varying from N/32 to N/2048, give the same value for K_i for the ethylate ion in these *ideal solutions*, but *apparently different uncorrected values* for K_i and K_m in the more concentrated solutions.

7. We are investigating these peculiarities, or abnormalities, of these concentrated solutions (absolute alcohol) as rapidly as possible by attempting to measure their physical properties, especially the fluidities of the solutions by Bingham's methods, the effect of added salts on the reaction velocities, and the probable extent of the solvation (alcoholation) of the reacting constituents by Washburn's methods. These *physical factors* and the *electronic phenomena* probably play a role having far greater significance than we can possibly understand with our present knowledge.

Johns Hopkins University
June 1, 1910

TREATISE ON GENERAL AND INDUSTRIAL INORGANIC CHEMISTRY. By ETTORE MOLINARI, Professor of Industrial Chemistry to the Society for the Encouragement of Arts and Manufactures of Merceology at the Commercial University Luigi Bocconi at Milan. Third Revised and Amplified Italian Edition. Translated by ERNEST FEILMANN, B.Sc., PH.D., F. I. C. With 280 illustrations in the text and one chromolithographic plate and two phototype plates. Philadelphia: P. Blakiston's Son & Co. 1912. Pp. xvi + 704. Price, $6.00.

In the preface to the first edition of this book the author says: "General and inorganic chemistry should no longer be a simple and arid expression of fundamental laws and of the properties of innumerable known substances, but should possess a soul which brings it into contact with the vital activities around which it clings. In a course of general inorganic chemistry all the applications which have been made of the fundamental laws and of the properties of substances should be studied. The chemical text-books which have been used until now do not correspond sufficiently to these requirements, and it is only since a couple of years that attempts have been made to reform this state of affairs and to carry into practice the improvements which have been urgently demanded from several quarters.

"I am far from believing that this book may be considered as a treatise on chemical technology but it is my conviction that industrial chemistry must start from the foundations of general chemical culture embodied in this treatise, in order to enter into all the technical and economic conditions of manufacture of the more important compounds, and in order to place the young chemist in a position to assume the direction of and collaboration in our chemical industry with more success and utility."

Whatever views one may hold in regard to the value of instruction in chemical technology in the early stages of the student's course, all will agree that statements in regard to applications of substances and principles add to the interest of the treatment, and they are, therefore, desirable. It is in statements of this kind that the book before us differs most markedly from other text-books now in use.

In Part I those subjects which are generally treated of under the head of theoretical chemistry are taken up. Here will be found interesting, though brief, discussions of the fundamental laws and principles of chemistry: osmotic pressure; electrolytic dissociation; equilibrium in heterogeneous systems and the phase rule; radioactivity and the unity of matter.

The real value of the book depends upon the statements concerning industrial applications. No book known to the writer of this notice can at all compare with it in this respect, and every chemist will be interested in the statements bearing upon these subjects.

While turning the leaves I find on page 133 this, which may be well known to many, but is certainly not known to many others: "In the Russo-Japanese War (1904–05) the Russians found it convenient, in order to avoid the transport to and fro of heavy steel cylinders, of compressed hydrogen for their balloons on the field of battle, to produce hydrogen as required on the spot (in Manchuria) by the action of 30 per cent. caustic soda solution on aluminium scrap." * * * * "In the Boer War the British employed hydrogen compressed to 200 atmospheres in steel cylinders, and required fifty horses for the transport of all materials for a balloon of 400 cubic meters."

Under Sterilization of Water is found this statement: "Of all methods of sterilization proposed up to the present the safest and most economic is the treatment of the water with ozone. In 1891, Dr. Ohmüller first investigated the behavior of thevarious species of bacteria in the presence of slightly ozonized air and succeeded in showing that none of the pathogenic bacteria, especially when distributed in water, resisted the action of ozone, even when much diluted. The *Bacteria subtilis* (hay microbe) alone resists the action of ozone (and also a temperature of 110°), but it is a perfectly inoffensive organism, both for man and for animals.

"From that time the solution of the great problem of the sterilization of water only awaited the time when it would be possible to obtain ozone cheaply and in large quantity.

"To-day the solution of the problem is an accomplished fact and there are in Europe many important plants for the ozonization of water."

Twenty-six pages are given to the subject of sulphuric acid; ten and a half pages to the utilization of atmospheric nitrogen; eighteen pages to the element carbon in its different forms.

Another interesting illustration of the thoroughness of the author's method will be found under the head "Aluminium Silicate." The subjects treated of under this head are ceramic industry; porcelain; bricks and tiles; artificial bricks and stones; hydraulic mortar and cements; natural cements; Roman cements; natural and artificial Portland cements; manufacture of artificial cements; cement burning kilns; rotary kilns; cement testing; applications and statistics—twenty-five pages being taken for these subjects.

It is perhaps needless to add that iron in its various forms receives full treatment. The metallurgy of iron is discussed in twelve pages, and then follows a section on the micrography of iron and steel.

The latest statistics are given in an appendix and it is noted that in many cases these are brought down to the year 1911.

The book can be cordially recommended to all chemists.

I. R.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS (Braunschweig), M. DELBRÜCK (Berlin), J. M. EDER (Wien), H. FREUNDLICH (Braunschweig), P. FRIEDLAENDER (Darmstadt), C. HAEUSSERMANN (Ludwigsburg), A. HERZFELD (Berlin), EDV. HJELT (Helsingfors), K. A. HOFMANN (Berlin), G. KEPPELER (Hannover), E. KNECHT (Manchester), J. LEWKOWITSCH (London), A. MORGEN (Hohenheim), B. NEUMANN (Darmstadt), M. NIERENSTEIN (Bristol), P. RONA (Berlin), herausgegeben von RICHARD MEYER (Braunschweig). XXI. Jahrgang. 1911. Braunschweig: Druck und Verlag von Friedrich. Vieweg und Sohn. 1912.

The only change in the personnel of the editorial board of this Annual is the substitution of Professor Herbert Freundlich, of Braunschweig, for Dr. Sackur for the report on Physical Chemistry. The high standard of the publication is maintained, and as has been stated in previous notices it is indispensable for working chemists. It has the advantage of being brief and yet not so brief as to be indigestible. It is made up of the reports enumerated below:

I. Physical Chemistry. By Herbert Freundlich.

II. Inorganic Chemistry. By K. E. Hofmann.

III. Organic Chemistry. By Edv. Hjelt.

IV. Physiological Chemistry. By Peter Rona.

V. Pharmaceutical Chemistry. By Heinr. Beckurts.

VI. Chemistry of Foodstuffs. By Heinr. Beckurts.

VII. Agricultural Chemistry. By A. Morgen and G. Fingerling.

VIII. Fuels and Explosives. By C. Haeussermann.

IX. Metallurgy. By Bernhard Neumann.

X. Inorganic Chemical Industries. By Gustav Keppeler.

XI. Technology of the Carbohydrates. By A. Herzfeld and Herm. Zimmermann.

XII. Fermentation Industries. By M. Delbrück and O. Mohr.

XIII. Technology of Fats and Petroleum. By J. Lewkowitsch.

XIV. Chemistry of Tar and Dyes. By P. Friedlaender.

XV. Chemical Technology of Textile Fabrics. By Edmund Knecht.

XVI. Tanning. By M. Nierenstein.

XVII. Photography. By J. M. Eder and E. Valenta.

It is interesting to note that the longest section is that relating to Organic Chemistry. This occupies 123 pages; Physical Chemistry, 72 pages; and Inorganic Chemistry, 54.

I. R.

THE PRINCIPLES OF ORGANIC CHEMISTRY. By JAMES F. NORRIS, PH.D., Professor of Chemistry in Simmons College, Boston. International Chemical Series. HENRY P TALBOT, PH D., Consulting Editor. New York and London: McGraw-Hill Book Co. 1912. Pp. v + 566. Price, $2.50.

In the preface the author states: "This book is the outcome of a number of years' experience in teaching the elements of organic chemistry to classes of beginners in the subject. In it an attempt has been made to emphasize the fundamental principles of the science and to describe in some detail the organic compounds of practical importance. The substances considered have been selected from this point of view. As a consequence, many compounds of interest to the more advanced student have been omitted; the space gained in this way has been devoted to a fuller consideration of the more important typical reactions of organic compounds and the applications of the science have been treated at greater length than is customary in elementary text-books."

The order followed in discussing the various classes of compounds differs from that usually made use of in text-books of this kind. The author refers the radicals to hydrogen as the standard, calling those more basic than hydrogen positive and those more acid negative. Alcohols consist, then, according to him, of a positive radical in combination with the hydroxyl group and acids of a negative radical with this group. This view leads the author to consider acids *immediately after the alcohols have been described.* Then he takes up ethers, anhydrides and esters, compounds which, according to him, contain, respectively, two positive radicals, two negative radicals and one positive and one negative radical linked to oxygen. The classing of these three types of compounds together makes it possible, according to the author, to bring out the relationship between the properties of compounds and the character of the radicals they contain. The consideration of alkyl and acyl halides and of amines and amides in a similar way, according to him, facilitates markedly the study of the properties of these compounds. Unfortunately the result of this is that the alkyl halides, usually considered, on account of their simplicity, immediately after the hydrocarbons, are not taken up till Chapter XII and the consideration of the amines is postponed till Chapter XI.

The carbohydrates, fats, proteins and dyestuffs are treated much more fully than is customary in elementary text-books on organic chemistry. In Chapter XVII the methods used in the identification of organic substances are described and illustrated by examples. The experience of the author has convinced him that this kind of work has great pedagogical value and can replace profitably a part of the synthetic work of the student. Problems are given at the end of most of the chapters and the author states that the solution of such problems has been found of the greatest value to the student.

The book contains some errors, which are, however, not very serious and can be easily corrected in a later edition of the book. For example, on page 27, it is stated that magnesium may be used instead of zinc in the preparation of methane from methyl iodide and then it is stated that magnesium methyl iodide with water yields methane, magnesium hydroxide and magnesium iodide, whereas the reaction of zinc methyl iodide with water is given as follows:

$$Zn\langle{}^{CH_3}_{I} + HOH = Zn\langle{}^{OH}_{I} + CH_4$$

On page 61 it is stated that isoprene is converted into India rubber when it is treated with concentrated hydrochloric acid. It is very doubtful whether India rubber can be made in this way. At any rate, Tilden, who claims to have made India rubber by this method, has never been able to repeat the experiment and no other worker in this field has ever succeeded in making India rubber in this way.

The statement on page 522 that fluorone dissolves in alkalies to form fluorescent solutions is incorrect. Fluorone is insoluble in alkalies and advantage is taken of this fact to separate it from phenolphthalein. On page 523 it is stated that *chrysolin* or *uranin* is benzylfluorescein. *Chrysolin* is *probably* the disodium salt of benzylfluorescein, while *uranin* is the disodium salt of fluorescein. Eosin, mentioned on the same page, is not tetrabromofluorescein, but the disodium salt of that compound. The formula given for guanine on page 556 is incorrect.

The book is well printed and bound and contains a large amount of information. In the opinion of the reviewer, however, it is not adapted to the use of beginners in organic chemistry.

W. R. O.

THE PREPARATION OF ORGANIC COMPOUNDS. By E. DEBARRY BARNETT, B.Sc. (LOND.), A.I.C. With 50 illustrations. Philadelphia: P. Blakiston's Son & Co. 1912. Pp. xvi + 310. Price, $2.75.

In this book "the author has aimed at giving a general out-

line of the methods actually employed in preparing organic compounds, and thus providing not only a laboratory manual, but also a book which may be used as a companion volume to the usual theoretical text-books."

In the first chapter, apparatus, methods of manipulation and reagents are considered and then follow methods for the preparation of the various hydrocarbons and their derivatives in the succeeding chapters. No attempt is made to separate the preparation of the paraffin hydrocarbons and their derivatives from those of the aromatic compounds or the preparation of the unsaturated from the saturated compounds. The first experiment given is the preparation of ethylbenzene and shortly after this comes that of menthene and dipentene. From this it will be seen that the book is not intended or at any rate is not suited to those beginning the subject of organic chemistry. The descriptions of the processes given are generally very brief and for the most part taken literally from the original articles without any change or explanations, so that unless a student has already had some experience in working in an organic chemical laboratory he would hardly be able to use this book profitably. A considerable number of the preparations have been taken from the patent literature and the author states that by this means he hopes to familiarize the academic chemist with a much neglected branch of the literature. The book seems to contain but few errors and these are of minor importance. For example, on page 39, the formulas for dipentene hydrochloride and dipentene both lack a hydrogen atom, and on page 239 it is stated that: "Some *diazo-chlorides*, however, notably those of sulphanilic and naphthionic acids, are insoluble in water and separate out." Of course, this is wrong, for neither sulphanilic acid nor naphthionic acid form diazonium chlorides when diazotized. They give inner ammonium salts, the diazonium sulphonates. The author uses diazo-salt and diazo-chloride quite frequently where it would be better to say diazonium salt. In some cases the directions are manifestly too brief. For example, in the preparation of phenolphthalein no mention is made of fluorone, nor is the student told how to remove it from the phenolphthalein which it always accompanies.

The book is well printed and bound and has a good index. In the hands of advanced students of organic chemistry it will probably be of value. W. R. O.

Modern Research in Organic Chemistry. By F. G. Pope, B.Sc. (Lond.), F.C.S. With 261 Diagrams. London: Methuen & Co., Ltd. Pp. xii + 324. Price, 7 s. 6 d.

The book is divided into nine chapters entirely independent

of each other: The Polymethylenes, 38 pages; the Terpenes and Camphors, 62 pages; the Uric Acid or Purine Group, 24 pages; the Alkaloids, 75 pages; the Relation between the Color and Constitution of Chemical Compounds, 22 pages; Salt Formation, Pseudo Acids and Bases, 23 pages; the Pyrones, 30 pages; Ketenes, Ozonides, Triphenylmethyl, 22 pages; the Grignard Reaction, 20 pages.

In the first four chapters and in that on the pyrones, a large number of representatives of the groups of compounds under discussion are taken up and the reactions, synthetical and analytical, by which their constitutions have been determined, are given. Structural formulas are used lavishly. To the reviewer, it seems that if fewer compounds had been discussed and the relationship of one to the other brought out more clearly, the result would have been a more interesting book. As it now stands, the reader soon wearies of the multitude of equations and formulas given; it is not a book which can be read for the pleasure of it, and its chief use will probably be found in that it gives briefly and diagramatically the series of reactions by which the constitutions of the compounds discussed have been worked out. The chapter on the Grignard reaction suffers from the same disadvantage.

The other chapters are more interesting. That on the relation between color and constitution takes up briefly the chromophore and auxochrome theories, the quinonoid theory, Baeyer's "carbonium valency," and Baly's "isorropesis" theory. In the chapter on salt formation are discussed, all too briefly, oxonium and carbonium salts. Hantzsch's views on pseudo acids and bases receive somewhat more extended and adequate treatment. The few pages devoted to ketenes, ozonides and triphenylmethyl will be read with interest. These chapters could have been made longer at the expense of the others without detracting from the value of the book.

References to the more inportant articles bearing on the subject are appended to each chapter. Although published in 1912, the book seems to have been written almost entirely about 1909, as very few pieces of work done since then are given mention.

In the first edition of a book involving so many equations, typographical errors are bound to occur, but the number of such errors found in the present volume is inexcusably large.

C. A. R.

THE INTERPRETATION OF RADIUM, being the Substance of Six Free Popular Experimental Lectures delivered at the University of Glasgow. By FREDERICK SODDY, M.A., F.R.S., Independent Lecturer in Physical Chemistry and Radioactivity in the University of Glasgow. With Illustrations. Third Edition, Revised and Enlarged. New York: G. P. Putnam Sons. 1912. Pp. xvi + 284. Price, $2.00.

This interesting book is a statement in popular and somewhat flowery language of the well-known facts in connection with radioactivity. There are some defects to which the reviewer must call attention. On page 18 we read, "The juxtaposition of radioactivity and transmutation is not a fanciful one, because it will appear, as we proceed, that the two processes are most intimately connected." The spontaneous production of helium from the radium emanation bears no relation to transmutation of the elements, as I have repeatedly pointed out. The spontaneous production of one substance from another, at a rate which can not even be varied, by any means known to man, is one thing; and the production of one element from another by artificial means, which is what the alchemists meant by 'transmution,' is obviously an entirely different matter. The latter problem is apparently as far from being solved as it was in the days of the alchemists.

One other point in reference to the book as a whole. The facts of radioactivity would to-day be just so many empirically established facts, without any possibility of explanation, were it not for the work of Sir J. J. Thomson on the electron, which preceded the discovery of radioactive phenomena. If Thomson had not shown that the simplest chemical atom is tremendously complex; if he had not overthrown the older chemical conception of the atom that it was a simple ultimate unit of matter, we could never have had the present theory of radioactivity.

Thomson not only showed that the atom is complex, but in what its complexity consisted, in rapidly moving electrons. This made possible the theory of the *unstable atom*, which underlies the explanation of all radioactivity. There is not enough stress laid upon this fact, and not enough credit given Thomson by the author of this book. With this exception the defects in the work are of minor consequence. H. C. J.

EXPERIMENTAL RESEARCHES ON THE SPECIFIC GRAVITY AND THE DISPLACEMENT OF SOME SALINE SOLUTIONS. By J. Y. BUCHANAN, M.A., F.R.S., Chemist and Physicist of the Challenger Expedition. Reprinted from the Transactions of the Royal Society of Edinburgh, Vol. XLIX, Part 1. Edinburgh: Neill & Co., Limited. 1912. Pp. 227. Price, 7 s. 6 d.

In this monograph the author gives a detailed account of his important investigations on the determination of the specific

gravity of salt solutions. Since the year 1871, when he was appointed chemist and physicist to the "Challenger" expeditions, he has been more or less continuously engaged in studying precise methods for the determination of specific gravity. After considering the relative merits and defects of all of the well-known methods for the determination of density he chose the hydrometric method since, to quote his own words, "the hydrometer appeared to be the only type of instrument which furnished *directly* the information demanded, namely, the specific gravity of the water, and that with the exactness required when the variations of specific gravity are so small."

It is a matter of no little surprise to learn that this experimenter has brought the hydrometric methods to such a high state of perfection that it is possible to determine specific gravities to six places of decimals, with a probable error of less than three units in the sixth place. Tables are given of the specific gravities of solutions of the chlorides, bromides, iodides, chlorates, bromates, iodates, and nitrates of the alkali metals, together with similar data for some salts of the metals of the alkaline earths.

In one of the last sections of the work the author calls attention to a remarkable state of unrest observed in supersaturated solutions of calcium chloride before crystallization. This is one of the most interesting chapters of the monograph and has an important bearing upon the mechanism of crystal formation.

Chemists and physicists owe Mr. Buchanan a debt of gratitude for his work in refining the hydrometric method for the determination of specific gravity and also for the very valuable tables he has compiled. This monograph should be in the possession of every one who has occasion to make precise determinations of specific gravity.

FREDERICK H. GETMAN

WATER, ITS PURIFICATION AND USE IN THE INDUSTRIES. By WILLIAM WALLACE CHRISTIE, Consulting Engineer. New York: D. Van Nostrand Company. 1912. Pp. xi + 219. Price, $2.00.

This book, intended primarily for engineers, contains descriptions of processes and apparatus for the softening, purifying, removing of oil and measuring of water. Great pains has apparently been taken by the author to make these descriptions not only accurate but readily understood, and in most instances he has admirably succeeded. He is not so fortunate in his treatment of so-called "Impurities of Water," which discusses the mineral constituents. For example, the impression is given that calcium and magnesium occur in water as the normal carbonates. The chapter on "Drinking Water" might be improved by rearranging and sorting the data; and

the statement on page 2 that "Albuminoids and free ammonia get into water supplies through the run-off water and give rise to many epidemics" is somewhat surprising.

A chapter containing information which might be useful to the engineer dealing with water supplies and water works is well put together. The text is amply illustrated with excellent cuts. As a whole, the book should be of considerable value to engineers. G. F. NORTON

DAS ERDÖL, SEINE PHYSIK, CHEMIE, GEOLOGIE, TECHNOLOGIE AND SEIN WIRTSCHAFTSBETRIEB. In fünf Bänden. Herausgegeben von C. ENGLER, o. ö. Professor an der Techn. Hochschule zu Karlsruhe, und H. v. HÖFER, o. ö. Professor an der Montanistischen Hochschule zu Leoben, unter Mitwirkung von verschiedenen Gelehrten. I. Band, zweite Abteilung mit Tabellen-Beilage. Leipzig: Verlag von S. Hirzel. Pp. xvii + 262. Price, M. 22.00.

This deals first with a brief description of the properties and physical characters of all the known crude petroleums, arranged by countries, completing Part III. Part IV considers the congeners of petroleums, ozokerite, asphalt and natural gas. Part V treats of the physiological action of petroleum and its products.

The tables give analyses of typical oils from all the various countries.

The first volume has already beeen reviewed.[1] A. H. GILL

FATTY FOODS: Their Practical Examination. A Handbook for the Use of Analytical and Technical Chemists. By E. RICHARDS BOLTON, F.C.S., Consulting Analyst and Technical Chemist, and CECIL REVIS, Chief Chemist, Messrs. Welford & Sons, Ltd. Philadelphia: P. Blakiston's Son & Co. 1913. Pp. x + 371. Price, $3.50.

In this volume the examination of fatty foods is regarded entirely from the edible standpoint. The authors presuppose a general knowledge of the chemistry of fats and oils and then give methods for the analysis of a large number of these compounds, from both animal and vegetable sources, together with the results which they have obtained by the outlined method.
F. P. UNDERHILL

INDEX TO VOLUME XLIX

The Index to Volume XLIX of THIS JOURNAL will appear in the July number.

[1] THIS JOURNAL, **48**, 472.

INDEX TO VOL. XLIX

AUTHORS

SUBJECTS

FORMULAS

C_1-GROUP

1 II

C_2-GROUP

2 II

2 III

C_3-GROUP

3 II

C_4-GROUP

4 II

4 III

C_5-GROUP

5 II

C_{10}-GROUP

10 III

10 IV

C_{11}-GROUP

11 II

11 III

C_{12}-GROUP

12 III

12 IV

C_{13}-GROUP

13 III

C_{18}-GROUP

18 II

18 III

C_{19}-GROUP

19 II

19 III

C_{21}-GROUP

21 II

C_{23}-GROUP

23 II

23 III

ERRATA

P. 82, l. 2 from the bottom, the formula should be $C_4H_2O_4Ag_2$.

P. 313, l. 23, the formula should be HOCOOH.

P. 461, l. 4, the formula should be $C_6Cl_4O_2C_5(OC_2H_3O)_2Cl_5$.

P. 503, l. 3, $K_N\frac{(\alpha)^2}{V}$ should be $K_m\frac{(\alpha)^2}{V}$.